

ION EXCHANGE

1. Introduction

Ion exchange is a process in which cations or anions in a liquid are exchanged with cations or anions on a solid sorbent. Cations are interchanged with other cations, anions are exchanged with other anions, and electroneutrality is maintained in both the liquid and solid phases. The process is reversible, which allows extended use of the sorbent resin before replacement is necessary.

Many naturally occurring inorganic and organic materials have ion-exchange properties. Synthetic organic ion-exchange resins became available in the late 1930s with the introduction of phenolic-type products. Styrenic resins appeared in the mid-1940s, and acrylic resins about 20 years later. The ion-exchange market of the early to middle 1990s is dominated by the styrenic resins, but acrylic resins are becoming increasingly important. Phenolic-based resins have almost disappeared. A few other resin types are available commercially but have not made a significant impact. Inorganic materials retain importance in a number of areas where synthetic organic ion-exchange resins are not normally used. Only the latter are discussed here. This article places emphasis on the styrenic and acrylic resins that are made as small beads. Other forms of synthetic ion-exchange materials such as membranes, papers, fibers (qv), foams (qv), and liquid extractants are not included (see EXTRACTION, LIQUID-LIQUID; MEMBRANE TECHNOLOGY; PAPER.).

The primary application for ion exchange is the softening and deionization of water. The remaining applications include waste treatment (qv), catalysis (qv), purification of chemicals, plating, hydrometallurgy, food processing (qv), and pharmaceutical uses. Because ion-exchange resins are insoluble polymeric acids and bases, these resins are also useful in removing acids and bases from gaseous streams via the neutralization of functional groups.

Weak and strong acid-type resins are for removal of cations and are called cation exchangers. Weak and strong base resins remove anions and are called anion exchangers. In addition to these four resin types, there are specialty resins used in applications where higher specificity for certain ions under challenging conditions is a critical factor.

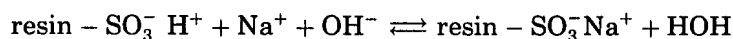
Continuous columnar operation of ion-exchange systems is preferred over batch operation. Each column must be taken off-stream periodically to remove the adsorbed ions and restore the resin to the ionic form required for the adsorption (qv) step. In this sense, a columnar ion-exchange operation is not continuous. Installations are usually designed with multiple units to assure a continuous flow of the process stream when one or more of the columns require regeneration. In those installations where the ion-exchange system is not required throughout the day, regeneration is scheduled during idle time and the system requires fewer ion-exchange units. Continuous operation has been approached in a number of designs by moving resin, or vessels containing resin, in a direction opposite to the flow of liquid. Some of these approaches have been abandoned; others are increasing in popularity.

All aspects of ion exchange covered herein are presented in much greater detail in the numerous books devoted to the subject (1-7).

2. Types of Ion-Exchange Resins

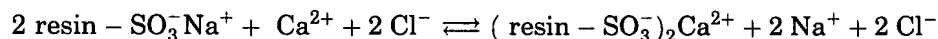
Ion-exchange resins are categorized by the nature of functional groups attached to a polymeric matrix, by the chemistry of the particular polymer in the matrix, and by the porosity of the polymeric matrix. There are four primary types of functionality: strong acid, weak acid, strong base, and weak base. Another type consists of less common structures in specialty resins such as those which have chelating characteristics.

2.1. Cation-Exchange Resins. Strong acid. Strong acid cation-exchange resins have sulfonic acid groups, $-\text{SO}_3^- \text{H}^+$, attached to an insoluble polymeric matrix. When the functional groups are in the hydrogen form and the resin is in contact with a liquid containing other cations, hydrogen ions leave the solid phase and enter the liquid phase as they are replaced by cations from the liquid phase, for example,



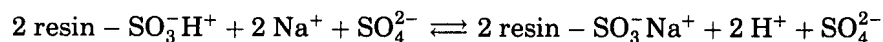
The liquid phase is free of Na^+ and the functional groups of the resin are converted to a sodium salt. Multivalent cations are removed in a similar manner. Electric charge neutrality must be maintained in both the liquid and solid phases.

It is not always necessary for the resin to be in the hydrogen form for adsorption of cations, especially if a change in the pH of the liquid phase is to be avoided (see also HYDROGEN-ION ACTIVITY). For example, softening of water, both in homes and at industrial sites, is practiced by using the resin in the $^+$ form.



Sodium ions are displaced from the resin by calcium ions, for which the resin has a greater selectivity.

In many industrial applications, strong acid cation-exchange resins are used in the hydrogen form to process liquids containing low concentrations of salts.



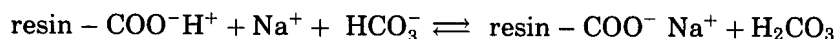
This is commonly referred to as a salt splitting reaction. The resin's selectivity for Na^+ is greater than it is for H^+ . Anions are removed in a similar manner with an anion-exchange resin.

Ion-exchange reactions are reversible. A regeneration procedure restores the resin to the ionic form it was in prior to the adsorption step. Reversibility of reactions allows resins to be used many times before replacement is considered. Strong acid cation exchangers are returned to the hydrogen, H^+ , form with dilute hydrochloric acid [7647-01-0] or sulfuric acid [8014-95-7]. Other mineral acids are used at times. However, the safety, cost, and methods of disposal must be thoroughly reviewed before using other acids. A 4% acid concentra-

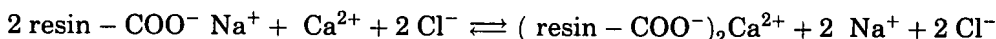
tion is common. The use of higher or lower concentrations is dependent upon the process, the design of the system, and the potential for forming insoluble salts of the acid.

Weak Acid. Weak acid cation-exchange resins have carboxylic acid groups, $-\text{COOH}$ attached to the polymeric matrix. Although not as versatile in process applications as the strong acid resins, these resins are included in numerous systems where higher operating capacities and greater ease in regeneration can be used advantageously.

Weak acid cation exchangers have essentially no ability to split neutral salts such as sodium chloride [7647-14-5]. On the other hand, an exchange is favorable when the electrolyte is a salt of a strong base and a weak acid.

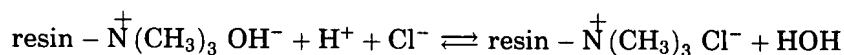


The sodium form of weak acid resins has exceptionally high selectivity for divalent cations in neutral, basic, and slightly acidic solutions.



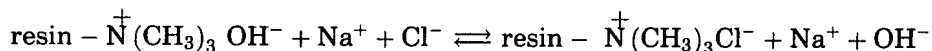
The selectivity is so great that reversal of the reaction to restore the resin to the Na^+ form is not practical using NaCl solutions at any concentration. Regeneration with dilute acid, followed by conversion of the resulting H^+ form to the Na^+ form with dilute sodium hydroxide [1310-73-2], is the preferred alternative.

2.2. Anion-Exchange Resins. Strong Base. Strong base anion-exchange resins have quaternary ammonium groups, $-\text{N}^+(\text{R})_3\text{OH}^-$, where R is usually CH_3 , as the functional exchange sites (see QUATERNARY AMMONIUM COMPOUNDS). These resins are used most frequently in the hydroxide form for acidity reduction.

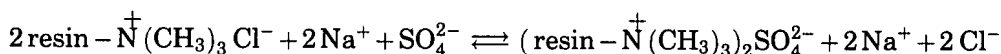


Hydroxide ions [14280-30-9] are released by the resin as anions are adsorbed from the liquid phase. The effect is elimination of acidity in the liquid and conversion of the resin to a salt form. Typically, the resin is restored to the OH^- form with a 4% solution of NaOH .

The hydroxide form is also used in salt splitting applications.

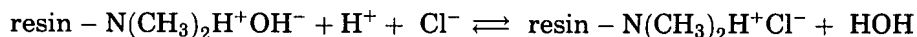


Salt forms of a strong base anion exchanger are used to remove other anions for which the resin has greater selectivity.



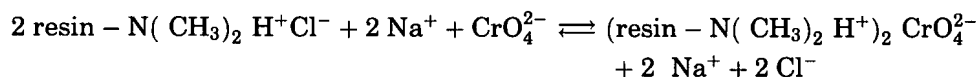
Weak Base. Weak base anion-exchange resins may have primary, secondary, or tertiary amines as the functional group. The tertiary amine

$-\text{N}(\text{CH}_3)_2$ is most common. Weak base resins are frequently preferred over strong base resins for removal of strong acids in order to take advantage of the greater ease in regeneration.



Most weak base anion exchangers adsorb weak organic acids such as formic acid [64-18-6] and acetic acid [64-19-7], but do not remove weak organic acids such as carbonic acid [463-79-6] or silicic acid [7669-41-4].

Weak base resins when in the free base (hydroxyl) form are not capable of splitting neutral salts such as sodium chloride. Salt forms of weak base resins release anions to the liquid phase if other ions for which the resin has a greater selectivity are present.



This interchange of ions is similar to that of the strong base resins.

2.3. Chromatographic Resins. The ion-exchange reactions illustrated are typical of those which occur in numerous industrial installations when the primary objective is the removal of ions, acids, or bases from a liquid stream. These same resins are useful for chromatographically separating ions having the same valence. Ion-exchange resins have a different selectivity for each ion. Sometimes these differences are too small for a separation to occur. In addition, other factors including flow rate, column design, and resin properties usually govern the success or failure of a chromatographic separation (see CHROMATOGRAPHY).

Although not of commercial interest, consider a separation of Ca^{2+} and Mg^{2+} . A solution containing low concentrations of each cation is fed slowly and continuously to a column containing a strong acid-type cation-exchange resin in the Na^+ form. At first the solution leaving the column contains only Na^+ because it is displaced from the resin as Ca^{2+} and Mg^{2+} are adsorbed. As flow continues, Mg^{2+} appears in the effluent, but not Ca^{2+} . Because the selectivity of the resin is greater for Ca^{2+} than for Mg^{2+} , Ca^{2+} displaces the Mg^{2+} previously adsorbed by the functional groups. As flow continues and the column becomes loaded, Ca^{2+} appears in the effluent at increasing concentrations along with Mg^{2+} .

Chromatographic separations are not limited to ionic constituents. For example, glucose [50-99-7], $\text{C}_6\text{H}_{12}\text{O}_6$, is separated from fructose [57-48-7], $\text{C}_6\text{H}_{12}\text{O}_6$, when using a strong acid cation exchanger in the Ca^{2+} form. The functional groups hinder the forward movement of each sugar at a slightly different rate as a solution containing both sugars flows slowly through a column containing the resin. Water [7732-18-5] is fed alternately with the sugar solution to aid in developing the separation. Glucose precedes the appearance of fructose in the effluent (8), indicating fructose is prevented in its forward motion by the resin to a greater degree than is glucose.

Resins having other types of functional groups are growing in importance. Resins that have metal chelating capabilities include those containing iminodiacetic acid [142-73-4] or aminophosphonic acid sites (9). Resins having thiol functionality are interesting for adsorption of metals which form sulfide precipitates. Resins containing an *N*-methylglucamine [6284-40-8] functionality are selective for boron [7440-42-8].

3. Manufacture of Resins

The production of ion-exchange resins is a multiple step process. It begins with the polymerization of monomers to form solid intermediate copolymers that are insoluble in both water and solvents. The copolymers are functionalized during additional steps in different reactors from those used for copolymer production. Conversion to another ionic form may be required after functionalization is completed. All resins are thoroughly rinsed with water to cleanse them of residual chemicals. Excess water is removed by vacuum filtration prior to packaging. Complete removal of all water by drying is unusual. Packaging in fiber drums is common. Alternative containers include metal drums, bulk boxes and bags, and smaller plastic, paper, and burlap bags. Polyethylene [9002-88-4] liners are used as a barrier between containers and water-containing resin.

Manufacture of ion-exchange resins has traditionally been a batch process. Significant progress was made more recently in the development of a continuous process for the manufacture of copolymer beads. However, as of this writing (ca 1994) is it not used by all manufacturers. Moreover, those companies having continuous processing capabilities do not use it for all ion-exchange products.

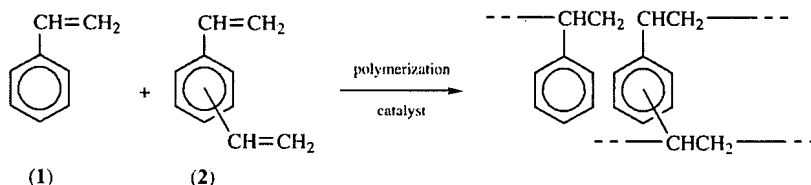
3.1. Copolymerization. The chemistry of the resin matrix, the type and degree of porosity, the particle size, and the particle size distribution are established in the copolymerization step. Formulations and operating procedures must be strictly followed. Reaction vessels must be well designed. Mistakes made during copolymerization are rarely corrected during functionalization.

The procedure of forming copolymers dates back to the early 1940s when only phenolic resins were available. Copolymers were produced by bulk polymerization of phenol [108-95-2] and formaldehyde [50-00-0]. Because the resulting solid product had the shape of the vessel in which polymerization took place, it had to be reduced to smaller particles by crushing and grinding before being functionalized. A new chemistry, and a new process, appeared in the mid-1940s when it was learned that styrene [100-45-2] could be copolymerized with divinylbenzene [1321-74-0] (DVB) by a suspension polymerization process, and that the small, hard copolymer beads could be functionalized (10,11). These styrenic resins eventually replaced the phenolic resins in practically all applications. Since then, another chemistry has evolved to complement the styrenic resins in process applications. These are the acrylic resins which are functionalized copolymers of an acrylic monomer and DVB produced by the suspension polymerization technique.

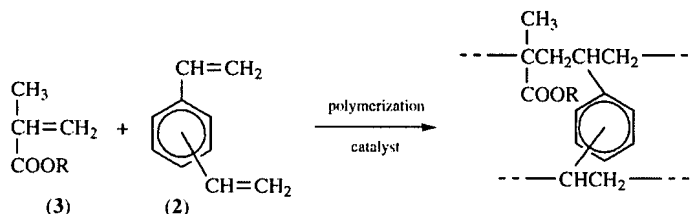
Design of copolymer reactors became more complex with the introduction of suspension polymerization. The size and uniformity of the ion-exchange resin to be produced from a copolymer was now dependent on the size and uniformity of a

liquid monomer mix dispersed as small droplets in an aqueous medium. The shape, size, and speed of mixers, as well as baffling to control fluid flow within the reactors, became critical factors. These reactors must be closed to the atmosphere, and they must be fitted with appropriate piping and valves to allow rapid transfer of organic and aqueous phases from other tanks to the reactor, and to allow rapid removal of a copolymer slurry when the reaction is over. The reaction kettles are jacketed which provides a means for raising and lowering temperatures during polymerization. Careful selection of materials of construction assures long life, minimizes downtime for maintenance, and guards against contamination of the liquid and aqueous phases with elements which may interfere with the preferred rate of polymerization.

The organic and aqueous phases are prepared in separate tanks before transferring to the reaction kettle. In the manufacture of a styrenic copolymer, predetermined amounts of styrene (1) and divinylbenzene (2) are mixed together in the organic phase tank. Styrene is the principal constituent, and is usually about 90–95 wt% of the formulation. The other 5–10% is DVB. It is required to link chains of linear polystyrene together as polymerization proceeds. DVB is referred to as a cross-linker. Without it, functionalized polystyrene would be much too soluble to perform as an ion-exchange resin. Ethylene-methacrylate [97-90-5], and to a lesser degree trivinylbenzene [1322-23-2], are occasionally used as substitutes for DVB.



Formulations for acrylic copolymers involve monomers such as acrylic acid [79-10-7], methacrylic acid [79-14-4], or esters of these acids. Formation of a copolymer from a methylmethacrylate ester (3), where DVB serves as the cross-linker, gives the structures:



The fraction of DVB used in the monomer mix is governed by the required performance characteristics of the ion-exchange resin. The higher the percentage of DVB, the greater the number of sites at which polymeric chains of styrene, or acrylic monomer, are linked. High DVB levels increase the tightness of the polymer matrix and lessen the ability of ions or other solutes to migrate through the resin phase. Thus the porosity decreases as the cross-linking increases. When

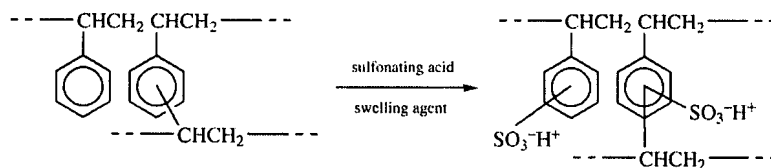
the organic phase contains only the monomers that participate in polymerization, the copolymers and resins produced from them are described as having a microporous or gel-type porosity. It is a porosity which cannot be measured by conventional methods. A different type of porosity, macroporous (also called macroreticular), is formed by incorporating a solvent along with the monomers in the organic phase. That solvent should have low aqueous phase solubility and must not participate in the polymerization reaction. When the organic phase is dispersed into the aqueous phase, the solvent is distributed throughout each droplet. The solvent, which remains with the hard copolymer beads during polymerization, is not bound to the resin matrix because it did not react with either monomer. Displacement of the solvent from the copolymer, or removal by vaporization, yields a copolymer with a measurable pore volume and pore size distribution. Both pore volume and distribution are dependent on the solvent and the amount incorporated in the original monomer mix.

The aqueous phase into which the monomer mix is dispersed is also prepared in a separate tank before transferring to the copolymerization kettle. It contains a catalyst, such as benzoyl peroxide [94-36-0], to initiate and sustain the polymerization reaction, and chemicals that aid in stabilizing the emulsion after the desired degree of dispersion is achieved. Careful adherence to predetermined reaction time and temperature profiles for each copolymer formulation is necessary to assure good physical durability of the final ion-exchange product.

Continuous processes for copolymer production were developed initially for the microporous resins. The system generally involves injecting the monomer mix into the aqueous phase through orifice plates. Droplet size is controlled by the diameter of the holes in the plate and the rate at which the monomer is injected into the aqueous phase. The continuous process produces copolymer beads which have greater uniformity in size than those produced in batches.

3.2. Functionalization. Copolymers do not have the ability to exchange ions. Such properties are imparted by chemically bonding acidic or basic functional groups to the aromatic rings of styrenic copolymers, or by modifying the carboxyl groups of the acrylic copolymers. There does not appear to be a continuous functionalization process on a commercial scale.

Strong Acid Cation Exchangers. All strong acid-type resins are made from styrene-DVB copolymers, with the exception of a minor quantity of phenolic resin. Batch sulfonation using commercial strength sulfuric acid [8014-95-1] is common.



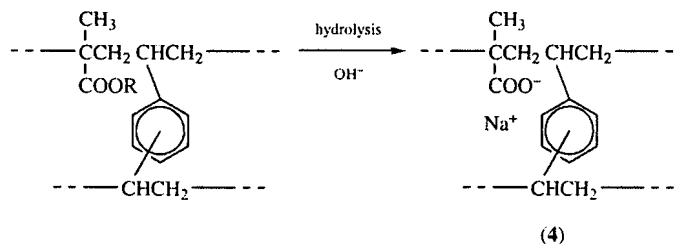
As in copolymerization, time-temperature profiles are followed closely in order to attach $\text{-SO}_3\text{H}$ groups to aromatic rings throughout the resin particle. Aromatic rings at the core of the beads are not as accessible as those closer to the surface. Sulfonation is usually carried out in a solvent such as ethylene dichloride [107-06-2] or propylene dichloride [78-87-5]. It can be accomplished without the

solvent. Appearance and physical stability of sulfonated products produced in the presence of a solvent are generally superior to resins sulfonated in the absence of a solvent. On the other hand, more environmental problems are associated with sulfonation in the presence of solvents. Whichever process is used, very little acid is consumed relative to the total amount in the reactor. Separation of a highly acidic liquid from the resin after functionalization must be approached with care. This liquid can be displaced with an acid of lower concentration. Otherwise, a dramatic change in the acid concentration results in rapid swelling and subsequent cracking of the resin particles. Recycling or reuse of acids is limited by the lowering of the acid concentration and by the increase in concentration of organic impurities.

Commercial demand for strong acid resins is greatest for those having microporous properties and a copolymer DVB content of 8%. Resins having greater cross-linking are generally preferred in processes where significant oxidative attack is expected because these are more resistant to deterioration. Resins functionalized from copolymers with less than 8% DVB are used in a variety of nonwater treatment applications where a more open polymeric matrix provides a better pathway for large ions and compounds migrating to functional groups within the resin particles. Macroporous cation exchangers usually have 12 to 25% DVB. They are particularly useful in applications where oxidative attack is severe. They are also beneficial in nonaqueous systems. A substantially larger number of functional groups, or exchange sites, are available along the internal surfaces present in macroporous-type resins, compared to just those sites on the outer surface of an unswollen microporous resin.

Corrosion of reactors used for functionalization and in pipes and valves along transfer lines for sulfuric acid is a problem that results in maintenance shutdowns. Sufficient agitation is needed to keep the resin beads fluidized during sulfonation. As for copolymer kettles, transfer lines should be sufficiently large to allow reasonably rapid transfer of liquids and resin slurries.

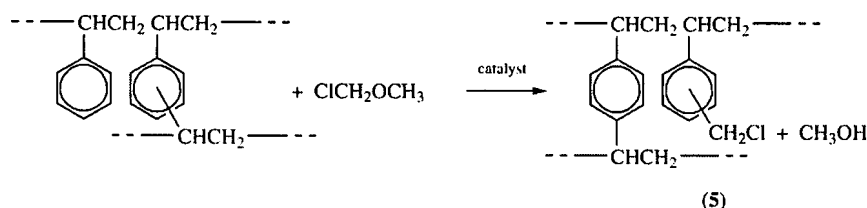
Weak Acid Cation Exchangers. The synthesis of weak acid cation exchangers is a one-step process when acrylic acid or methacrylic acid is copolymerized with DVB. If an acrylic ester is used as the monomer instead of an acrylic acid, the ester groups must be hydrolyzed after polymerization using either an acid or base (NaOH) to give the carboxylic acid functionality, or the sodium salt (4) of it.



The market for weak acid cation exchangers is much less than that of strong acid resins. As a consequence, fewer resin variations are available commercially. Very little published information is available concerning the degree

of cross-linking. Most weak acid resins have a macroporous structure, although the pore volume is significantly less than that of the strong acid resins.

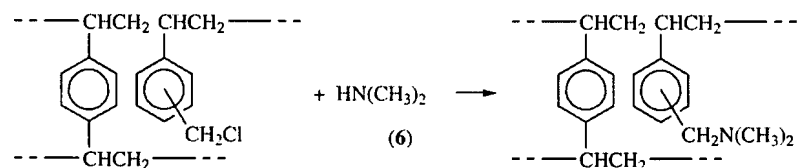
Weak Base Anion Exchangers. Both styrenic and acrylic copolymers can be converted to weak base anion-exchange resins, but different synthetic routes are necessary. Styrene-DVB copolymers are chloromethylated and aminated in a two-step process. Chloromethyl groups are attached to the aromatic rings (5) by reaction of chloromethyl methyl ether [107-30-2], $\text{CH}_3\text{OCH}_2\text{Cl}$, with the copolymer in the presence of a Friedel-Crafts catalyst such as aluminum chloride [7446-70-0], AlCl_3 , iron(III) chloride [7705-08-0], FeCl_3 , or zinc chloride [7646-85-7], ZnCl_2 .



The presence of bis(chloromethyl) ether [542-88-1], $\text{ClCH}_2\text{OCH}_2\text{Cl}$, in chloromethyl methyl ether generally results in additional secondary cross-linking when the chloromethyl groups at each end of the molecule combine with aromatic rings on two separate polystyrene chains. The amount of secondary cross-linking is dependent on the catalyst and the reaction parameters. As a consequence, copolymers synthesized specifically for the manufacture of anion exchangers tend to have a lower DVB content than copolymers used in the production of strong acid cation exchangers since the cumulative cross-linking has an effect on the performance properties of the ion exchanger.

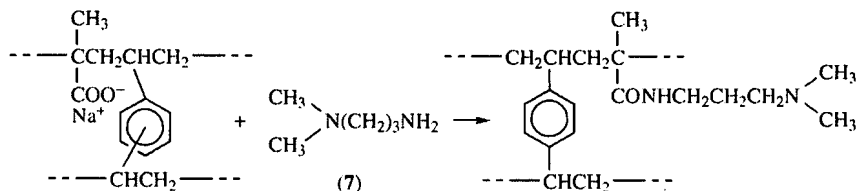
The chloromethylation reaction and the steps associated with its preparation and transfer to the reaction vessel are the most hazardous procedures in the manufacture of any ion-exchange resin. Bis(chloromethyl) ether and chloromethyl methyl ether are recognized carcinogens. Chloromethyl methyl ether is manufactured on site from methanol [67-56-1], or methylal [109-87-5], and formaldehyde. Some ion-exchange resin plants have a separate facility. Others produce it in the same kettle used for the chloromethylation reaction. Leaks in pipe joints, valves, and reaction vessels cannot be tolerated. Most if not all resin manufacturers have converted older processing facilities to fully automated systems. Buildings in which the reactions occur are placed under negative pressure. Personnel are not permitted in the production building unless protective masks and clothing are worn. Bis(chloromethyl) ether and chloromethyl methyl ether remaining after completion of the chloromethylation reaction are recycled or completely destroyed before the resin is aminated.

Functionalization is completed by aminating the chloromethylated copolymer with either primary or secondary amines. Dimethylamine [124-40-3] (6) is generally preferred, especially in the synthesis of the macroporous anion exchangers.



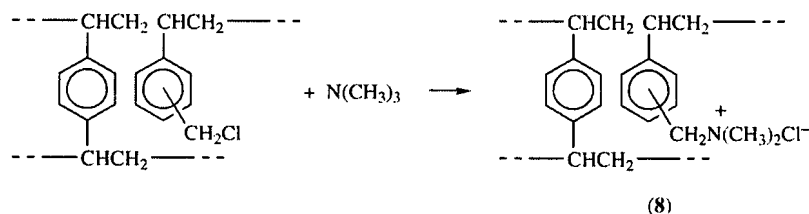
Polyamines, such as diethylenetriamine [111-40-0] are used at times in the synthesis of microporous weak base resins to achieve significantly higher capacity. However, these resins generally have lower physical and chemical stability than resins prepared from primary or secondary amines.

The acrylic weak base resins are synthesized from copolymers similar to those used for the manufacture of weak acid cation-exchange resins. For example, under appropriate temperature and pressure conditions, a weak acid resin reacts with a polyfunctional amine, such as dimethylaminopropylamine [109-55-7] (7) to give a weak base resin with a tertiary amine functionality.



Both the styrenic and the acrylic weak base resins are used in industrial applications for the same purposes, primarily the removal of acidic components in liquid streams. The styrenic weak base resins are more stable at temperatures over 37°C than the acrylic resins. On the other hand, the acrylic resins are more hydrophilic and tend to adsorb and release large molecular weight constituents more effectively than the styrenics. Levels of cross-linking are not usually disclosed by resin manufacturers. The variety of resins available is not as great as for the strong acid cation exchangers.

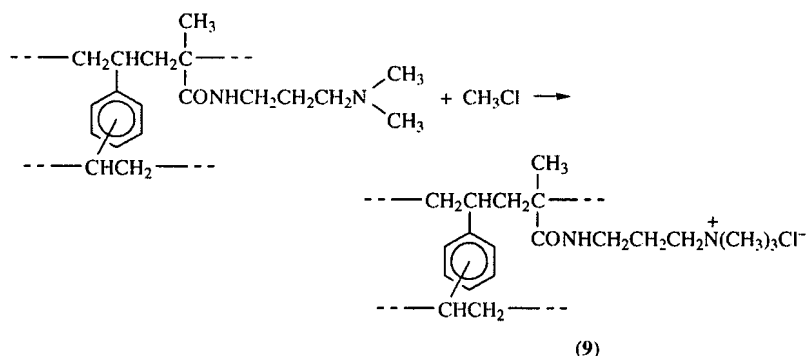
Strong Base Anion Exchangers. As in the synthesis of weak base anion exchangers, strong base resins are manufactured from styrenic as well as acrylic copolymers. Those based on copolymers of styrene and divinylbenzene are chloromethylated and then aminated. These reactions are the same as for the styrenic weak base resins. The essential difference is the amine used for amination. Trimethylamine [75-50-3], $\text{N(CH}_3)_3$, and *N,N*-dimethylethanolamine [108-01-0], $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}$, are most commonly used. Both form quaternary ammonium functional groups similar to (8).



Styrenic resins with this structure are commonly called Type I strong base anion exchangers (8) in the water treatment industry. Those aminated with dimethylethanolamine are referred to as Type II anion exchangers. These groups are slightly less basic than those of the Type I resins. As a consequence, anions are not held as tightly and they are replaced more efficiently by hydroxide ions when regenerated with NaOH solutions. Type II resins have lower chemical and thermal stability than Type I resins. Higher molecular weight amines such as triethylamine [121-94-8] and tributylamine [102-82-9] are used occasionally to make strong base resins which have enhanced selectivity for ions such as nitrate [14797-55-8], NO_3^- , over other ions normally present in water supplies and wastewaters. However, the mobility of ions through the resin matrix and the exchange capacity decrease as the size of the amine used for amination increases.

Low molecular weight amines are volatile and extremely odoriferous. They are removed from the atmosphere of the manufacturing facilities by scrubbing to comply with environmental regulations. An amine odor is common with packaged anion-exchange resins even though the resins are thoroughly washed before pack-out. Odor is most common for strong base resins aminated with trimethylamine, and when in the hydroxide form.

Acrylic strong base anion exchangers (9) are synthesized from acrylic weak base resins. The tertiary amine groups are converted to a quaternary ammonium functionality by reaction of chloromethane [74-87-3], CH_3Cl , and the weak base resin.



Referring to this quaternary structure in acrylic resins as Type I is controversial. Many of the properties are similar to those of the Type II styrenic resins. Precautions regarding chemical and thermal stability are generally the same for

acrylic strong base resins and the Type II styrenics. In addition, the ability to remove adsorbed ions during regeneration is about the same for the acrylic resins and Type II resins. This supports a suggestion that the basic strength of the $-N(CH_3)_3$ group on the acrylic is not as strong as the same group on the styrenic Type I resin, but more like the $-N(CH_3)_2CH_2CH_2OH$ on the Type II resins.

Acrylic anion exchangers are frequently preferred over the styrenic resins for removal of high molecular weight organic acids present in surface water supplies and in other process streams. Compounds such as these are not completely removed during the regeneration step. The accumulation of these compounds with increased cycles of use is referred to as organic fouling. The more hydrophilic structure of the acrylic resins provides a less complex pathway for the organic compounds to migrate out of the resin during regeneration, and organic fouling is minimized.

A simplified schematic layout of an ion-exchange production facility is presented in Figure 1. Layouts vary from one company to another and are significantly more complex when recycle of streams and environmental controls are incorporated in the schematics.

Separate kettles and backwash towers are frequently used to convert ion-exchange resins from one ionic form to another prior to packaging, and to cleanse the resin of chemicals used in the functionalization reactions. Excess water is removed from the resin prior to packaging by a vacuum drain. Both straight line filters and towers or columns are used for this purpose.

4. Physical and Chemical Properties

Ion-exchange resins are used repeatedly in a cyclic manner over many years, and deterioration of both physical and chemical properties can be anticipated. Comparison of the properties of used resin with those of new resin is helpful to learning more about the nature and cause of deterioration (12). Corrective action frequently extends the life of the resin. Comparison of properties must always be made with the resin in the same ionic form.

4.1. Particle Shape and Size. With few exceptions, resins are supplied as small, round beads having a diameter between 0.3 and 1.2 mm. Some resins are reduced to a smaller size by grinding to satisfy specific requirements in applications for electric power generation (qv) and pharmaceuticals (qv).

Resin size is dependent on two factors. One of these is the method by which the copolymer beads are formed, and the other is related to the exchange kinetics within the beads. Copolymer beads are made by batch-wise suspension of a liquid monomer mix in an aqueous medium or by a continuous jetting technique. In either case, formation of beads larger than 1 mm in diameter is difficult to achieve without agglomeration. Large beads are preferred for pressure drop advantages in columnar operations. However, large beads are subject to a greater rate of breakage than those having a smaller size.

Migration of ions to functional groups within the resin particles is slow compared to the aqueous or organic liquid phase surrounding the particles. The most

efficient ion-exchange processes occur when most of the functional groups can be accessed within a short contact time between liquid and resin. The larger the particle size, the greater is the time required to utilize groups deeper in the particles. Thus, the smaller the bead, the better. However, the smaller the size, the greater the pressure drop. A particle size range spanning 0.3–1.2 mm in diameter has been a compromise between acceptable kinetics and pressure drop.

A Gaussian distribution of particle size is the result of copolymer manufactured by suspension polymerization. A jetting process produces beads with more uniform particle size. The uniformity coefficient is a numerical method of indicating closeness of all beads to the same size.

Wet screening using a set of U.S. Standard sieves (297, 420, 595, and 841 μm openings; 50, 40, 30, and 20 mesh, respectively) is the standard procedure for determining particle size distribution. The volume percent retained on each is recorded. The cumulative percent retained is plotted as the abscissa and the screen opening in mm as the ordinate on log-log probability graph paper. The best straight line is determined. The uniformity coefficient is defined as the ratio of the screen opening that retains 90% of the particles to the opening that retains 40%. The effective size is defined as that screen opening which retains 90% of the particles, as obtained from the same graph. If both the uniformity coefficient and effective size are available for a batch of resin, the approximate distribution by sieve opening can be calculated.

Wet screening is being replaced in many laboratories by instruments that use a photosensor to record the diameter of each particle in a water suspension as that suspension flows past the sensor.

4.2. Density and Specific Gravity. Density generally pertains to the bulk, or pack-out, weight of wet resin per unit volume. The density is characteristic of the resin and is dependent on the copolymer structure, the degree of cross-linking, the nature of the functional groups, and the ionic form of those groups. A change in density after extended use is a signal that chemical degradation has occurred. The density of most cation exchangers is in the 800–900 g/L range, whereas most anion exchangers are in the 640–740 g/L range.

The specific gravity generally refers to the value determined for wet resin when using a pycnometer. Values range from about 1.04 to about 1.25. Cation exchangers have a greater specific gravity than anion exchangers.

4.3. Porosity. The structure of ion-exchange resins is either microporous or macroporous. Microporous resins are more commonly referred to as gel or gelular-type resins. Porosity of this type resin cannot be measured by standard techniques. Gel resins are porous when the particles are swollen with water or another solvent. There is no porosity when the resin is dry. Microporosity is inversely proportional to the degree of cross-linking. Large ions migrate through a low cross-linked resin faster than through the less porous, higher crosslinked resins.

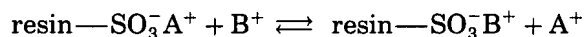
Macroporous resins are also called macroreticular. Macroporous resins have a measurable porosity. It does not disappear when the resin is dry. Porosity is more dependent on the solvent used when manufacturing the copolymer than on the degree of cross-linking.

4.4. Capacity. Capacity is a measure of the quantity of ions, acid, or base removed (adsorbed) by an ion-exchange material. The quantity removed is directly correlated with the number of functional groups. Capacity is reported in several different ways, but requires further definition because the word by itself does not cover all situations. Total capacity is a measure of all the functional groups on a resin and is recorded on a weight as well as a volume basis. A manufacturing objective is to place at least one functional group on each aromatic ring in styrenic-type resins. As a consequence, the degree of cross-linking has little effect on the total dry weight capacity, as shown in Figure 2, for strong acid cation exchangers in the hydrogen form. Dry resins swell when wet with water. The amount of swelling decreases as the degree of cross-linking increases. For this reason, the effect of cross-linking on total volumetric capacity is more demonstrative, as is also shown in Figure 2 for the same resins.

Operating capacity, also called the working capacity or column capacity, is a measure of the quantity of ions, acids, or bases adsorbed, or exchanged, under the conditions existing during batch or columnar operation. Because the adsorption process is terminated in most commercial applications before all functional groups have been utilized, the operating capacity is less than the total capacity. Operating capacities vary from one installation to another, even though the same resin might be used at each location. Such variations are the result of differences in composition of the stream to be treated, flow rate, effluent quality that triggers shutdown for regeneration, and regeneration conditions. Examples of the dependence of operating capacity on the degree of regeneration and resin type are illustrated in Figure 3 for typical weak base and strong base anion exchangers.

The steeper slope for the weak base resin is an indication that these resins are regenerated with greater efficiency, or ease, than strong base resins. Strong base anion exchangers do not release anions as readily as weak base anion exchangers. For each incremental increase in the amount of chemical used for regeneration there is a greater incremental increase in the operating capacity of the weak base resin than the strong base resin. If two resins have the same total capacity but differ in basic strength and are regenerated under identical conditions, the resin having the lower basicity is restored more completely to a regenerated form and has the higher operating capacity. A similar analogy can be made for weak and strong acid cation exchangers.

4.5. Selectivity. A significant exchange of ions does not occur unless the functional group of the resin has a greater selectivity for ions in solution than for ions occupying the functional group, or unless there is a mass action effect, as in regeneration. Selectivity coefficients have been reported in numerous publications for both cations and anions. These coefficients are determined at very low concentrations using the two specific ions in question. In the following reaction, for example, the cation-exchange resin removes cations B^+ from solution in exchange for A^+ on the resin because the selectivity of the resin for B^+ is greater than for A^+ .



At equilibrium, the selectivity coefficient (K_A^B) for B over A is determined from the following equation:

$$K_A^B = \frac{\bar{m}_B}{\bar{m}_A} \cdot \frac{m_A}{m_B}$$

where m and \bar{m} are the ionic concentrations of the ions in the solution and resin phase, respectively. Selectivity for ions having the same charge usually increases as the atomic weight increases ($\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$ and $\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$). Selectivities for divalent ions are greater than for monovalents. Higher selectivity for trivalent and tetravalent ions does not necessarily follow the expected progression. The following examples (Table 1) have been chosen to illustrate the effect of type of strong base functionality and mole fraction of chloride [16887-00-6] in a two-component anion system on selectivity constant (13).

The need to know selectivity coefficients precisely is rarely necessary in industrial applications. However, knowledge of relative differences is important when deciding if the reaction is favorable or not. Most ion-exchange applications are for the removal of more than one ionic species. In water softening, it is important to know that a cation exchanger has a greater selectivity for divalent cations than for monovalent cations. It is not critical to know the resin prefers Ca^{2+} over Mg^{2+} . In deionization, it is important to know that all cations normally present in a water supply are preferred by a strong acid cation exchanger over a hydrogen ion [12408-02-5], H^+ , and that all anions are preferred over OH^- by a strong base anion exchanger. Differences in selectivity coefficients take on greater importance in chromatographic separations where flow rates are much slower to allow more time for ionic species to separate as the liquid flows through the resin bed.

Selectivity differences increase as the degree of cross-linking of a resin increases, but these differences are relatively minor. Structural composition of the functional groups has a much greater effect on the magnitude of selectivity differences, as is illustrated for softening of water supplies. The sodium form of either a strong or a weak acid cation exchanger removes Ca^{2+} and Mg^{2+} from water effectively. However, the selectivity of the weak acid resin is so much greater that very concentrated solutions of NaCl do not reverse the reaction during the regeneration step, as it does for the strong acid cation exchanger. Even greater selectivity for divalent cations is observed for resins having aminophosphonic acid or iminodiacetic acid functionality.

4.6. Kinetics. The degree to which an ion-exchange reaction is completed depends on a number of factors which include contact time, ionic concentration, degree of cross-linking, and temperature. Contact time and concentration are interrelated and most important for a successful ion-exchange process. The impact of temperature increases as the viscosity increases. In columnar operations, short contact times associated with high flow rates are acceptable when the concentration of ionic constituents in the influent stream is very low. At higher electrolyte concentrations, the contact time must be increased. If contact time is too short, functional groups on or near the surface are converted to another ionic form sooner than groups deeper in the resin particles. The net result is the appearance of ions that were to be adsorbed in the effluent sooner than would have occurred with a longer contact time, and lower utilization of all the resin's capacity. Flow rates of 8 to 40 bed volumes (BV)/h ($1-5 \text{ gal/min/ft}^3$)

are common in conventional water treatment systems where ionic concentrations might be as high as several hundred mg/L. Slower flow rates should be considered for ionic concentrations exceeding 500 mg/L. For those systems which have ionic concentrations in the $\mu\text{g/L}$ range, as in condensate polishing and similar recycle applications, flow rates are usually significantly greater than 40 BV/h.

A hypothetical illustration of the ion concentration–flow rate effect is presented in Figure 4. Consider two identical columns operating under the same conditions, except for the ionic concentration of the influent solution. One stream, curve C, has a concentration x , and the other $2x$. Once ions appear in the effluent, they increase in concentration as more solution passes through. These curves, showing effluent concentration vs the volume of solution treated, are called leakage curves. For purposes of this example, the column is shut down for regeneration when the effluent concentration is 5% of the influent concentration. If the stream having twice the concentration had no effect on the exchange rate, then the leakage curve would be represented by curve B. Only half the volume could be handled by the resin because the ionic concentration is twice as much. The operating capacities for columns having leakage curves represented by curves C and B would be the same. If the flow rate is too great to allow the migration of ions to exchange sites deeper in the resin particles, then a leakage curve such as curve A can be expected. The operating capacity is less in this example because the adsorption cycle is terminated when ions in the effluent reach 5% of the influent concentration. The lower capacity is represented by the difference in the volume processed to the 5% cut-off point by curves B and A.

Some industries practice ion exchange in nonaqueous systems. These solvents may cause resin particles to shrink or swell. Shrinkage has a negative effect on the kinetics, whereas swelling opens up the structure and improves migration of those constituents to be adsorbed. Microporous resins usually do not work well in nonaqueous systems because of the disappearance of porosity. Macroporous resins, however, are more satisfactory in these systems since porosity is retained even if the resins are dried completely. More functional groups on outer and inner surfaces are available for exchange as a result of the combined fixed porosity and relatively high surface area. Nevertheless, these systems are operated at slower rates to compensate for slower migration of ions, acids, and bases through organic solvent or process stream surrounding the resin particles.

Several aqueous systems should be considered in a similar manner. For example, in the selective removal of divalent cations from a saturated salt solution, the hydrated resin gives up a portion of its normal water content as it contacts the salt stream. In so doing, the particles shrink, and the inner pathways for ion migration become smaller.

4.7. Moisture and Water Content. Resins are thoroughly washed with water upon completion of manufacture and conversion (if necessary) to another ionic form. Excess water is removed by vacuum draining or filtration. Nevertheless, a significant quantity of water associated with the functional groups and adhering to the outer surface of the resin particles remains with the resin as it is discharged into shipping containers. No effort is made to dry the resin, except

in a few application areas, since the resins are used in aqueous processes in most installations.

Each resin has a characteristic water content dependent on the resin matrix, the structure of the functional groups, and the ionic form of those groups. Resins are packaged by weight and sold by volume. The dewatering operation prior to packaging is a critical step since removal of too much water is costly to the manufacturer, and removal of too little is costly to the buyer. Analyzing for water content is important to both the seller and user. The quantity of water contained by the resin is recorded on a percentage basis and determined by two methodologies. In each procedure, a small (ca 15 g) sample is removed from a larger composite sample collected during pack-out. In one procedure, the sample is accurately weighed before and after placing in a 105°C oven for at least 8 h. This procedure yields the moisture content typical of resin contained in the shipping containers. In the other procedure, a similar sample is soaked in water, then filtered under vacuum in a Buchner funnel prior to weighing before and after oven drying. The moisture content reported is a pseudoequilibrium value typical of the specific resin and its ionic form. If the value reported is either greater or lower than the expected range, all manufacturing steps need to be examined for deviation from the standard manufacturing procedure. Values determined by both methods rarely differ by more than 1%. A significant difference is an indication of a procedural change or malfunction of equipment in the plant dewatering step prior to packaging. Water content of strong base resins in the hydroxide form cannot be determined in the same manner since thermal degradation with additional weight loss occurs at 105°C.

4.8. Swelling and Shrinking. Ion-exchange resins shrink or swell reversibly as they are converted from one ionic form to another. The degree of change is dependent on the resin matrix, the functional group, and the ions adsorbed by the functional groups. For similar matrixes, the magnitude of volume changes decreases as the level of cross-linking increases. Resins in contact with solutions having a high electrolyte concentration shrink as water is drawn from the resin. These reswell when in contact with more dilute solutions. Wetting the resins with nonaqueous solvents causes shrinking or swelling, depending on the solvent. Swelling is greatest for weak acid cation exchangers (up to 100%). Weak base anion exchangers may swell as much as 50%. Strong base resins swell about 15–25%. Strong acid-type resins swell the least and are usually in the 5–10% range.

The degree of swelling and shrinking is important for design of ion-exchange columns, especially for the location of the distributors used to disperse incoming fluids, and collect outgoing ones, evenly over the cross-sectional area of the resin bed. Once placed, these distributors are not adjustable. The upper distributor should be above (the lower one below) the resin bed, even in the bed's swollen form.

4.9. Hydraulic Properties. Both the resistance to liquid flow through a resin bed and the degree to which a resin bed expands during a backwashing step are important design factors for ion-exchange systems. These characteristics are also critical to those using the resins because movements of resins not only signal the existence of a problem but give indications as to the nature of the problem.

Pressure drop and hydraulic information for new resins are available from the resin manufacturer and the supplier of equipment.

Factors which have the greatest impact on pressure drop are the depth of the bed, flow rate, viscosity, temperature, and particle size. Pressure drop is also dependent on the hardness of the resin, or its ability to resist deformation when under compressive forces as in columnar systems with the process stream flowing down. Styrenic resins are more resistant to deformation than acrylics, and macroporous resins are more resistant than microporous. Minor increases in pressure drop as a result of bed packing are to be expected in lengthy downflow runs. Resins which have been used for a large number of cycles may yield a significantly higher pressure drop compared to those when the resin was new. These increases suggest problems with dirt, biological growth, or an increase in resin fragments within the column. Another cause may be oxidative attack of the resin which, in effect, makes it behave as a more compressible lower cross-linked resin.

Examples of pressure drop variation for new resin as a function of flow rate and water temperature are shown in Figure 5 for a standard styrenic strong acid cation exchanger. The lower pressure drop at the higher temperature is a reflection of water viscosity.

Backwashing is the upward flow of water through a bed of resin at a flow rate sufficient to fluidize the resin, but not so great that resin is carried out of the column with the exiting water. Resins are backwashed to remove dirt and resin fragments, to classify resin particles by size, and to relieve any packing that may have occurred with previous use. Frequency may be as great as once each cycle. Backwash times are 15 to 30 minutes, unless conditions require more time. Resin columns are designed with adequate space above the resin bed to allow 50–100% expansion during backwash. Each resin has a characteristic bed expansion profile which is dependent on the resin's specific gravity and particle size distribution. Severe accidental losses of resin occur during the colder months when the temperature of water used for backwashing is ignored. Lower temperature increases the water viscosity which increases the bouyancy effect on the resin particles. If the flow rate of the backwash water is not reduced, the bed expansion may be so great that resin particles leave the column with the exiting water. In warmer months, backwash flow rate should be increased. The dependence of expansion on flow rate and temperature is shown in Figure 6 for a strong acid cation exchanger.

Chemical Stability. Oxidants, such as dissolved chlorine [7782-50-5] in water supplies, react with synthetic ion exchangers to cause a loss of capacity, physical weakening of the resin, and partial solubilization of the resin. Anion-exchange resins are most prone to loss of functionality as the oxidant attacks and severs the linkage between nitrogen and carbon on the polymeric structure. In addition to this form of degradation, the functional groups of strong base anion exchangers partially convert to weak base groups through loss of one or more of the alkyl groups attached to the nitrogen. The net effect is loss of both strong base and total capacity with an increase in weak base capacity. Loss of functional groups from cation-exchange resins by oxidative attack is uncommon.

The point at which two polymeric chains are joined together by a cross-linker such as divinylbenzene, or sites where tertiary hydrogens are located in

the structure, are other locations for oxidative attack. In both cation- and anion-exchange resins, oxidative attack results in the removal of cross-linking. The moisture content is higher than when the resin was new. Resins having lesser amounts of cross-linking are more subject to physical deformation when under compressive forces than a resin with a greater amount of cross-linkage. Consequently, a gradual increase in pressure drop across the resin bed is to be expected as oxidative attack continues. In severe cases, the resin breaks into fragments. A resin that has undergone significant oxidative degradation releases small soluble fractions of the polymeric structure to the liquid phase, thus contributing to the biological oxygen demand (BOD). Such groups may or may not interfere with ion-exchange units that follow. An increase in the quantity of water to rinse the column after regeneration is another indicator of oxidative attack, especially for anion-exchange resins. The severance of functional groups leads to the development of carboxylic acid functionality. These groups are converted to the sodium salt when in contact with the NaOH used for regeneration. The water rinse which follows the regeneration step slowly hydrolyzes sodium ions from these groups causing the pH of the effluent to remain high for longer periods of time than realized with new resin.

The rate of oxidative attack is enhanced by the presence of metals such as iron [7439-89-6] and copper [7440-50-8] which serve as catalysts (14), by higher temperatures, and by higher concentrations of oxidants. The direct effect of each of these factors is a matter of opinion because all of the factors causing oxidative degradation are present at the same time but to varying degrees over the useful life of the resin. The tolerable limit for residual chlorine in a water supply is an example. At any concentration, the rate of attack is greater in warmer climates than in colder ones, all other factors being equal. A common recommendation is not to exceed 0.3 mg/L residual chlorine; others may recommend a 0.1 mg/L limit, and still others believe 1 mg/L is a safe upper limit. The oxidant concentration can be lowered before the process stream contacts the resin by standard procedures such as the use of carbon [7440-44-0] columns and the feeding of sulfite [14265-45-3].

Aside from low concentrations of oxidants found in most water supplies, the processing of chemical streams with much higher levels of oxidizing chemicals is practiced occasionally on an industrial basis. The potential dangers are generally recognized. Nevertheless, there is the potential for an uncontrolled reaction that releases heat which converts a liquid to a gas, resulting in the rupture of equipment in an explosive manner. Systems must be designed with appropriate detectors for abnormal performance, and with procedures that reverse or stop the reaction before it gets out of control.

Thermal Stability. Ion-exchange resins should not be used at temperatures above those recommended by the manufacturer. Exceptions are made when frequent replacement of resin is an economic advantage over the operating and capital cost of cooling and reheating the process stream. Functional groups are lost from both cation- and anion-exchange resins when the temperature limit is exceeded (15,16). The rate of loss increases exponentially as the temperature rises above the upper limit. Sulfonated cation exchangers can frequently tolerate temperatures up to 125°C (255°F). Strong base anion exchangers having a trimethyl quaternary ammonium structure can be used up to 77°C (170°F) in salt

forms and up to 60°C (140°F) in the OH⁻ form. Those strong base resins with a dimethylethanol quaternary ammonium structure and the acrylic anion exchangers are limited to about 40°C (104°F).

Physical Stability. Excessive pressure drop across the resin bed causes fragmentation of the beads. The point at which this occurs depends on the structure of the resin and in most systems is well above the pressure drop listed in product literature for water systems. Upper limits are about 7–9 kg/(cm²m) (30–40 psi/ft) for gel (microreticular) type resins in the 8–12% DVB range. If oxidative attack occurs during use of the ion-exchange resin the maximum pressure drop would be characteristic of a lower cross-linked resin. Resin breakage aggravates the pressure drop problem. Macroporous resins generally can tolerate somewhat higher pressure drop than gel-type resins (17). Gel-type resins are more resistant than macroporous resins to breakage caused by a shearing motion.

Resins shrink and swell as they are alternately put through adsorption and regeneration cycles. The larger the volume change and the shorter the time involved, the greater the potential for physical damage to the resin particles. In most applications, the greater potential for physical damage occurs during regeneration. However, similar effects occur in a few applications when regenerated resin is contacted with high concentrations of salts, as in the removal of impurities from those salt solutions. The appearance of cracks is the first sign of physical deterioration. Fragmentation into smaller irregularly shaped particles is a sign of further deterioration.

Resins should always be protected from freezing, although that may not always be possible. Generally, a few freeze–thaw cycles do not result in visual damage (cracking or fragmentation). Nevertheless, some weakening of the physical structure occurs because fragmentation is apparent if cycling continues. If operating conditions dictate a lengthy shutdown of the ion-exchange system and the resin columns are in an area that cannot be protected from freezing, the columns may be filled with typical antifreezes without damaging the resin. Neither glycol nor alcohol damage any of the standard cation and anion exchangers. Solutions of NaCl may also be used. When the units are returned to service, they must be thoroughly rinsed with water and, preferably, regenerated before using. The glycol or alcohol must be disposed of in an environmentally approved manner.

Transfer of resin from one vessel to another, as for regeneration, does not physically damage the resin as long as certain practices are avoided. The fluidity of the resin slurry and the linear velocity in transfer lines should be sufficient to keep all particles in suspension. Resin that settles can lead to plugging of the transfer line. Sharp bends in the transfer line should be avoided. If a pump is used for transferring the slurry, it should be a type that will not allow resin particles to be caught in valves when they close. Recessed impeller, peristaltic, and some diaphragm pumps are used in large industrial systems. Recommendations from someone knowledgeable in resin transfer is advised in order to avoid a costly installation that may cause rapid loss of resin through physical damage.

Radiation Stability. Numerous studies have been undertaken to define the effect of radiation on all types of ion-exchange resins. As expected, the more intense the radiation the greater the damage (18). Cation and anion

exchangers lose weight and capacity, cross-linking is removed, and water-soluble components are released if the radiation tolerance limits have been exceeded. The effects of gamma radiation have been studied more than other types of radiation.

5. Equipment

Ion-exchange systems in process applications may be batch, semicontinuous, or continuous. Batch operations are not common but, where used, involve a kettle with mechanical agitation. Injecting with air or an inert gas is an alternative. A screened siphon or drain valve is required to prevent resin from leaving with the product stream.

Semicontinuous and continuous systems are, with few exceptions, practiced in columns. Most columnar systems are semicontinuous since flow of the stream being processed must be interrupted for regeneration. Columnar installations almost always involve the process stream flowing down through a resin bed. Those that are upflow use a flow rate that either partially fluidizes the bed, or forms a packed bed against an upper porous barrier or distributor for process streams.

The lower section of a column with downward flow must have a distributor system that not only collects liquid evenly over the cross-sectional area, but also supports the resin bed and prevents resin from leaving the column. The traditional method has been to place a network of pipes with small holes drilled in them (a distributor) in a bed of graded gravel, sand, or anthracite coal, which supports the resin bed. While that practice continues, the trend has been toward other approaches. In one modification, the underbed is eliminated by securely wrapping the pipe elements with small mesh, noncorrosive screening. The size of the screen openings must be sufficiently smaller than the resin particles to avoid plugging. Blockage of the openings increases pressure drop and contributes to uneven or channeled flow. Special pipes formed by spirally winding triangular wire around supports, while carefully controlling the space between the flat side of the wire as it is wound, is another approach that is gaining acceptance. Perforated plates separating the resin from the distributor are used in other installations. Careful design of the distributor is essential, especially for the larger diameter units (see FLUID MECHANICS). If the linear flow rate near the wall of the column is substantially less than the midsection of the column, premature breakthrough, more frequent regeneration, and incomplete utilization of the rated operating capacity for the resin result.

The space immediately above the resin bed may or may not be filled with liquid in downward flow systems, depending on the design. If not filled, water entering the column from the top and impinging on the upper surface of the resin bed forms hills and valleys unless the flow is dispersed over the cross-sectional area. A distributor similar to the one used to collect resin below the bed, or splash plate, is placed a short distance above the resin bed to improve the distribution of the process stream flow.

A distributor is frequently installed at the top of the column for use during backwash. It collects water evenly and prevents resin from escaping the column

should unexpected surges develop in the water flow during backwash. Columns lacking an upper distributor or screen to prevent loss of resin should have an external system to prevent resin from being lost to the drain. It is referred to as a resin trap and may consist of a porous bag that fits over the outlet pipe or a tank designed to lower the linear velocity. Resin drops to the bottom of the tank and is returned to the column when convenient.

Mixed-bed columns contain an anion and cation exchanger which must be regenerated independently after separation by backwashing. When regeneration is performed in the same column, a distributor is installed near the expected interface of the resins following the backwash. The distributor is used to feed regenerating solutions, feed water, and to collect spent regenerant solutions. Again, distributor design is critical.

All columns, distributors, and ancillary hardware such as piping, valves, and pumps must be constructed of corrosion-resistant materials, or coated with an appropriate substance. All streams that contact the hardware during each step of the cyclic operation need to be considered in this selection.

Columns are designed to have a larger internal volume than the quantity of resin they will contain. The extra space is to provide the necessary volume for a fluidized bed during backwash. Most units are designed for the space above the resin bed (free-board) to be between 50 and 100% of the packed resin bed. Small columns are, on occasion, designed for one-use applications. Since backwashing is of no importance, there is a tendency to fill the unit with as much resin as possible. That practice can be hazardous, especially if the resin swells as a result of oxidative attack or through conversion from one ionic form to another.

Column dimensions vary considerably from one installation to another, depending on the application, total flow, and overall system design. If a tall narrow column and a short wide column contain the same amount of resin and process a stream at the same flow rate, the wide column will have a more favorable linear velocity and a lower pressure drop. However, bed depths cannot be too low, especially in the larger diameter units. Otherwise achieving uniform flow over the cross-sectional area of the column is impossible. The recommended minimum bed depth is about one meter. Bed depths over three meters are most common in applications involving catalysis and chromatographic separations. Serious consideration should be given to the use of several columns in parallel in place of one very large unit, especially when a system cannot be shut down when regeneration is required.

Feed systems utilizing gravity are rarely used. Line pressure is usually adequate for small systems. Auxiliary pumps are required in larger systems to assure proper flow through all units and to avoid uneven flow should line pressure decrease as other demands for water or the process stream occur elsewhere in the facility.

Regenerating streams require dilution with water before contacting the resin. Eductor systems (which mix two fluids), in-line dilution, and separate storage tanks containing sufficient diluted regenerating solutions are commonly used. Appropriate measuring methods to assure that the correct concentration and volume of regenerant are transferred to the resin column should be incorporated in the system. A low concentration, or insufficient volume, adversely affects

the subsequent adsorption step. An unintentional higher concentration increases operating costs and magnifies a waste regenerant disposal problem.

6. Systems

Ion-exchange systems vary from simple one-column units, as used in water softening, to numerous arrays of cation and anion exchangers which are dependent upon the application, quality of effluent required, and design parameters. An illustration of some of these systems, as used in the production of deionized (demineralized) water, is presented in Figure 7.

A single-column installation is satisfactory if the unit can be shut down for regeneration. However, if flow of the stream being processed must be continuous, then two or more columns of the same resin must be installed in parallel. Regeneration of each is staged for different time periods.

Two columns, one containing a cation exchanger and one an anion exchanger, are required for a deionization process. The cation exchange unit must be a strong acid-type resin, except in more complex systems, and it must precede the anion-exchange unit. Placing the anion exchanger first (reverse deionization) generally causes problems with precipitates of metal hydroxides, assuming that cations that form these compounds are present in the entering water or process stream. The resin in the anion-exchange unit may be a weak base resin when removal of anions (silicate [12627-13-3], bicarbonate, fluoride, and others) of weak acids is not essential. Otherwise, the column must contain a strong base resin. An alternative is the installation of a third column, which contains the strong base resin, to be placed after the weak base anion-exchanger unit.

A column containing a mixture of cation- and anion-exchange resins is called a mixed bed. Although all types of resin have been considered for these units, the majority consist of strong acid cation and strong base anion exchangers. This system yields a higher quality deionized water or process stream than when the same resins are used in separate columns. Regeneration of a mixed bed is more complicated than of a two-bed system. A mixed bed containing the same total resin volume as in one of the two-bed columns lowers capital costs but must be regenerated at roughly twice the frequency. Mixed-bed units are preferred as final polishers for multiple-bed systems, recycling streams, condensate polishing, and other areas where the electrolyte concentration is in the low mg/L range or less.

Most ion-exchange columns are operated concurrently. Both the process stream and the regenerating solution flow through the resin bed in the same upward or downward direction. Downflow is more common. These streams flow in opposite directions in counterflow systems, as with downflow during the adsorption step and upflow during regeneration. Counterflow provides more efficient use of regenerating chemicals, a higher quality effluent, and higher operating capacity than is obtained with the same resins in concurrent systems. Installation costs are somewhat higher. Extra care must be taken during upflow regeneration since the higher specific gravity of the regenerating stream has a more buoyant effect on the resin particles. Fluidization lessens regeneration efficiency.

Weak acid cation exchangers are used in some deionization systems when bicarbonate alkalinity is higher than in normal water supplies. These resins are regenerated with much greater efficiency than strong acid resins, and operating capacity is higher. The column containing the weak acid resin is installed as the first in a chain or series of columns and removes all or part of the divalent cations, depending on the water composition. In an effort to reduce capital costs for each additional column placed in an ion-exchange system, some designs incorporate a layered bed approach. The two-bed weak acid column followed by a strong acid resin column is reduced to one column by layering the weak acid resin on top of the strong acid resin. A similar anion unit consists of a weak base resin layered on top of a strong base resin. The resins must not be mixed; otherwise, the advantages of using the weaker acidic or basic resin before the stronger version disappears. Much more care must be taken during backwash and regeneration to maintain the layers. Precipitation of calcium sulfate in the cation unit, and precipitation of silica in the anion unit, are potential problems during regeneration.

The most demanding requirements with respect to water quality are in the electronics industry and in very high pressure power plants (see ELECTRONIC MATERIALS; POWER GENERATION). Although mixed-bed units are recognized for giving practically complete removal of all ionic constituents, the mixed-bed unit will give off trace amounts if systems are not designed to approach 100% separation of the two resins before regeneration. Any cation-exchange resin remaining with the anion exchanger is converted to the sodium form when the anion exchanger is regenerated with NaOH. Likewise, any anion-exchange resin remaining with the cation exchanger is converted to the sulfate form when the cation exchanger is regenerated with sulfuric acid. Resins returned to service, after remixing, gradually release sodium ions or sulfate [14808-79-8] from resin exposed to the wrong regenerating solution. Dissociation of water provides the H^+ and OH^- needed for an exchange of ions to occur. Designs to overcome this problem include addition of an inert resin which occupies space between the anion and cation exchangers after backwash is completed. Special backwash towers have been designed for those systems which do not incorporate the inert resin. For example, a narrower diameter where the interface appears after separation minimizes the volume of resin which might contain some of each resin. That portion is saved for the next regeneration while resin above and below that zone is regenerated in other units.

Numerous efforts have been made to develop continuous ion-exchange systems in which resin moves intermittently or continuously in a direction opposite to the flow of all liquids during adsorption, backwash, regeneration, and rinse. These include resin-in-pulp (RIP) systems used in the uranium industry. Resin is placed in banks of baskets constructed from screens having a mesh size that allows ore particles in an acid or alkaline leached slurry to pass through. The baskets are dipped in and out of a trough through which the slurry passes. The banks of resin are advanced through water washes and regenerations by valving changes for solutions flowing through the troughs (4). In another design, a number of agitated tanks each containing an ion-exchange resin and the leached ore slurry are arranged in series. A vibrating screen is placed between each tank. A mix of resin and ore slurry flowing from a tank was pumped or air lifted to the

vibrating screen to separate resin from slurry. Resin moves in one direction to another agitated tank; slurry moves to a different tank in the opposite direction.

Another continuous system consists of columns having numerous perforated plates. Resin enters the top and liquid is pumped into the bottom. The liquid flow rate is adjusted to prevent resin from passing through the openings in either direction. Liquid flow is stopped for a short period to allow resin to drop through openings to the chamber below. Liquid flow resumes before resin can drop through more than one chamber.

A unit referred to as the Higgins Loop has been popular in water treatment, as well as other applications. Resin is pulsed at regular intervals around a rectangularly shaped loop. The diameter of the adsorption section is larger than that of the regeneration section.

A more recent approach, developed by Advanced Separation Technologies (Lakeland, Florida), involves the placement of a number of columns on a carousel that rotates constantly at an adjustable speed. Instead of having one tall fixed column, this system has one taller column which has been broken down into smaller columns on the rotating table. Each is connected in series which allows each column to be on the adsorption cycle beyond the normal breakthrough point typical of the larger column with no other column in series behind it. The number of columns in series during adsorption, backwash, regeneration, and rinse is variable. Liquids flowing into and out of each column change when the column reaches specific positions on the carousel as it rotates.

Many ion-exchange systems incorporate activated carbon [7440-44-0] columns to adsorb dissolved chlorine or high molecular weight organics. Reverse osmosis units are incorporated at times to lower the electrolyte concentration before ion exchange (see REVERSE OSMOSIS). Ultrafiltration (qv) units are installed to lower colloidal solids. Ultraviolet light systems are used to destroy microbiological organisms that tend to propagate in resins and recirculated water systems. Not only do these other water treatment procedures improve the quality of water produced but they also extend resin life.

Lead-lag or merry-go-round systems are more common in other areas of application than in water treatment. In these systems, two or more columns of the same resin are connected in series and the lead column is retained on the adsorption cycle beyond a typical breakthrough point. The lead column is removed for regeneration when the concentration of the effluent from that column is about equal to the influent concentration, or when leakage from one of the succeeding columns reaches a specified limit. The column that was second in line becomes the lead column. The column removed from the circuit is regenerated, rinsed, and then either put back into service in the last position or put on standby. These systems are most useful for recovery of valuable products, or for removal of toxic substances from waste streams. In either case, the objective is to use as much of the resin's total capacity as possible. Adsorbing more valuable product in this manner means a smaller amount of contaminating products are coadsorbed. When the system involves toxic substances, the regenerating stream is at higher concentration for precipitation or other means of disposal.

7. Cyclic Operation

Resins are seldom used once and discarded. Whether the system is run batchwise or in columns, the resin must be periodically removed from service and regenerated. An exception is the use of a resin as a catalyst in organic reactions. Each cycle consists of two principal steps, adsorption and regeneration, and one or more intermediate steps, rinse and backwash. Failure to use good practices results in poor cyclic performance.

7.1. Adsorption. Impurities are removed, or valuable constituents recovered, from a process stream during the adsorption step, which is also referred to as loading or exhausting the resin. Performance is rated primarily on meeting objectives for completeness of removal. Performance is also rated on operating capacity, frequency of regeneration, and operational costs. Variables affecting performance include resin selection, solution chemistry, operating conditions, and equipment design. All are interrelated in varying degrees. Completeness of removal improves by using a resin more selective for that constituent. Using a resin having a selectivity substantially greater than required for the process stream generally results in lower operating capacity, more frequent regenerations, higher operating costs, and higher capital investment. For example, strong acid rather than weak acid cation exchangers are used to soften water supplies. A change in the composition of the stream being processed has a dramatic effect on degree of removal unless regenerating conditions are changed. An increase in the ratio of sodium to divalent cations, or a decrease in the ratio of bicarbonate to sulfate, while maintaining the same total electrolyte concentration, lessens the degree of cation removal in a deionization process when using identical regeneration levels. Equipment must have good distributors for distribution and collection of the process stream flowing through the resin bed. Otherwise, significant quantities of resin have no opportunity to participate in the exchange process (channeled flow). Columns must be designed such that the flow rate through the resin bed is not too fast to accommodate the kinetic properties of the resin, nor too slow.

At times, the process stream flow must be increased after the initial installation to satisfy production demands. Depending on the magnitude of the increase, the existing system may or may not be able to handle the added flow. If it can, regeneration frequency must increase. Adding more resin to the column is often considered an alternative to installing another column. Resin addition lessens the space for backwash and may be a cause for poor column performance.

Degree of removal is usually shown graphically by plotting the effluent concentration as a function of the liquid volume processed. The concentration in the effluent is called leakage, and the plot is referred to as a leakage curve. Very low leakage is common for most ion-exchange installations. It may be below the analytically detectable limit. If above, it may be within acceptable performance requirements. Seeking significantly greater removal than required means higher chemical costs for regeneration because the regenerant level is higher than necessary. The adsorption step is usually terminated when the impurity level in the effluent exceeds a predetermined value, for example, greater than 5 or 10% of the influent concentration. The adsorption step might also be terminated

when the effluent conductivity (or resistivity) changes significantly, or when a predetermined time of operation or liquid volume has been reached.

7.2. Backwash. Process streams may contain small suspended particles that carry over from a previous processing step. Packed resin beds act as excellent filters for these particles although they are not recommended for this purpose. As suspended particles collect on top of the resin bed, and penetrate deeper down, pressure drop across the bed increases. In severe cases, uniform flow reverts to channeled flow with the liquid seeking the path of least resistance. In other situations, lengthy adsorption runs, though desirable, lead to an increase in pressure drop as the resin particles pack closer together. Both of these conditions are alleviated by backwash. Water is passed up through a bottom distributor at a flow rate sufficient to expand the resin bed by 50–100%, and exits the top of the column. No resin, other than a small amount that may have undergone physical degradation, should escape the unit as long as the column was designed to accommodate that degree of expansion. Tap water is usually of adequate quality for backwashing purposes. Backwash frequency varies from one installation to another. Water availability may be a controlling factor. In applications where the adsorption step exceeds several weeks, the service flow is, at times, interrupted to reverse the direction of liquid flowing through it, as a means to overcome the small degree of packing that took place.

As manufactured, most resins have a Gaussian-like distribution of particle size. Very few are as small as 0.3 mm or as large as 1.0 mm. Most are between 0.5–0.8 mm. A backwash before using new resin is common practice to assure uniform flow during the adsorption and regeneration steps. The backwash eliminates air pockets that may have formed while filling the column and sorts the beads such that the smaller sizes are at the top of the bed and the larger sizes at the bottom.

7.3. Regeneration. The regeneration step is also called elution. The word backflush is used in some areas but leads to confusion with the backwash step and should be avoided. Regeneration is of much shorter duration than the adsorption step. The combined time for backwashing, regeneration, and rinse is usually not longer than two hours. The time is shortened using a smaller volume of regenerating chemicals at a higher concentration, or by increasing the regenerant flow rate. Neither approach should be attempted until experiments have demonstrated that there will be no detrimental effects to overall operation of the ion-exchange system.

Ions have ample time to slowly migrate to the functional groups throughout the resin particles, including those at or near the core, during the adsorption cycle. If adequate time is not provided during regeneration for those same ions to migrate back out of the resin, then two problems, higher leakage and lower operating capacity, are experienced during the next adsorption step. Both conditions can be improved by lowering the regenerant flow rate (increases the contact time), or by using more regenerating chemicals. The latter approach is not only wasteful of regenerating chemicals but also increases waste treatment charges. Whereas the high electrolyte concentration of the regenerating solution provides a strong driving force for removal of ions from the functional groups during regeneration, the slow migration of ions through the resin particles is the main reason for patience in the regeneration step. Flow rates commonly used

for regeneration in terms of bed volumes (BV) are between 4–6 BV/h, but 2 BV/h is preferred in many cases. Higher flow rates are used occasionally. However, the advantages are questionable, except in those situations where precipitates might form while the regenerant stream is passing through the resin bed.

A regeneration level that gives 100% conversion of the resin to the regenerated form is economically unsound in almost all applications. The most cost effective regeneration level is the lowest one that will assure a column effluent meeting the required quality during the adsorption step. A higher regeneration level achieves the same goal with a somewhat higher operating capacity. Regeneration levels commonly used in industrial columns are between 1.6 and 3.2 g – equivalents/L resin (4–8 lb/ft³). The lower level of this range is about equal to the total capacity of strong acid cation exchangers (2.0 g – equivalents/L) and strong base anion exchangers (1.4 g – equivalents/L). Complete removal of all ionic constituents is rarely achieved with these resins even when the regeneration level is doubled. With weak acid and weak base resins, on the other hand, there is no advantage in using more than 10 to 15% excess acid or base over the equivalents of ions adsorbed during the previous cycle.

Cation exchangers are regenerated with mineral acids when used in the H⁺ form. Sulfuric acid [8014-95-7] is preferred over hydrochloric acid [7647-01-0], HCl, in many countries because it is less expensive and less corrosive. However, the use of hydrochloric acid is the best method of overcoming precipitation problems in installations which deionize water with high concentrations of barium or calcium compared to other cations. A 4% acid concentration is common, although sulfuric acid regenerations may start as low as 0.8–1% to minimize calcium sulfate [7718-18-9] precipitation. Phosphoric acid [7664-38-2] is rarely used because of cost and disposal problems. Nitric acid [7697-37-2] is to be avoided because it is known to cause catastrophic damage to resin, equipment, and personnel if appropriate controls and monitoring systems are not installed.

Strong base anion exchangers must be regenerated with sodium hydroxide [1310-73-2] when used in the OH⁻ form. Potassium hydroxide [1310-58-3] is a more expensive alternative. Weak base anion exchangers may be regenerated with solutions of ammonium hydroxide [1336-21-6], NH₄OH, or sodium carbonate [497-19-8], Na₂CO₃, although NaOH is more common. The most common concentration for basic regenerating solutions is 4%.

When strong acid cation exchangers are used in the Na⁺ form and strong base anion exchangers are used in the Cl⁻ form, they are regenerated with a 10% sodium chloride [7647-14-5], NaCl, solution. Other concentrations may be used, perhaps with some adjustment in flow rate.

The temperature for regenerating solutions is of little importance except when silica [7631-86-9] removal from a water supply is critical. The less complete the removal of silica from the resin during regeneration, the greater the leakage of it during the subsequent adsorption step. Silica is known to polymerize as it is adsorbed by anion-exchanger resins. As a consequence, depolymerization and solubilization of the silica must be improved by increasing the contact time with NaOH, by increasing the concentration of NaOH, or by increasing the temperature. The last approach is generally used. Temperatures should not exceed 60°C for the Type I resins, and 40°C for Type II and acrylic resins. Thermal degradation and the loss of functional groups occur when these temperatures

are exceeded. Elimination of silica from the resin bed is further improved by preheating the bed with warm water before injecting the NaOH solution.

A two-step regeneration is necessary in some applications. One step removes the adsorbed ions, and the second step places the functional groups in another ionic form. For example, weakly acidic cation exchangers are used in the sodium form to remove toxic metals, such as copper [7440-50-8] and nickel [7440-02-0], from neutral or slightly alkaline waste streams. The selectivity of the resin for these metals is so great that NaCl is ineffective for regeneration regardless of the concentration. The accepted route is to elute the metals with a 5–15% acid solution, which leaves the functional groups in the hydrogen form, and then follow with a dilute NaOH solution to convert the groups to the sodium form.

Mixed-bed resins cannot be regenerated until the two resins are separated by backwashing. Each resin is regenerated separately. The cation exchanger should not be in contact with the NaOH solution used for the anion exchanger. The anion exchanger should not be in contact with the acid solution used to regenerate the cation exchanger.

Recycling regenerating chemicals is a practical way to reduce chemical costs. However, the spent regenerating solutions exiting the column should not be recycled directly to the influent end of the column. In the regeneration of a cation exchanger with 4% acid, the acid solution is converted to a salt solution as it passes through the resin bed. The resin is converted to the H^+ form. If the spent regenerating solution were sent directly back to the column, the salt solution would remove the H^+ placed on the resin by the acid, and very little would have been gained. A profile of the spent regenerating solution as a function of the volume of solution passed through shows the start of a rapid drop in the salt concentration and a rapid rise in the acid concentration, after a volume of regenerating solution equal to 1.5–1.8 times the volume of the resin bed has passed through the bed. In recycling, collection of the spent regenerating solution should begin at some point after the peak salt concentration has been reached. The volume collected is saved for the next regeneration and is fed to the column prior to using fresh regenerating solutions.

7.4. Rinse. When transfer of the required volume of regenerating solution to the column has been completed, a small amount of regenerating solution occupies space immediately above the resin bed, between resin particles in the bed, and within the resin particles. It must be displaced with water before the column can be returned to the adsorption step. Rinsing should begin at the same flow rate as used during regeneration and continue at that rate until a volume of water equal to 1–2 bed volumes has been used. After that, the flow rate is increased to the rate normally used during the adsorption step, and continued at that rate until the effluent is of satisfactory quality, as determined by pH, conductivity, or resistivity. The water need not be at an elevated temperature unless the process stream is above ambient temperature.

7.5. Stability. Ion-exchange resins undergo chemical and physical deterioration at varying rates if appropriate care is not taken. Improvements have been made continuously in the physical stability of all synthetic ion exchangers. Since the chemistry of the polymeric structure and of the functional groups have not undergone modification since the introduction of styrenic and acrylic resins,

no changes are to be expected in oxidative stability except as to how it relates to the degree of cross-linking.

8. Shipping

Shipping resins in a water wet condition is standard practice. Removal of water by evaporative methods is expensive and not necessary for the majority of applications since they take place in aqueous systems. Dry resins (almost always strong acid cation exchangers) are required in several catalytic applications in the chemical industry. Water wet resins are packed out by weight and sold by volume. Containers consist of plastic bags and polyethylene-lined burlap bags for small packages in the 28 L (1 ft³) range. Larger containers consist of fiber drums lined with one or more polyethylene bags to prevent wetting and deterioration of the drum. Steel drum shipments are by request. Bulkbag (ca 850–1100 L) shipments have become more common since the early 1980s, especially where unusually large volumes of resin need to be transferred to processing equipment. Overhead space must be available for lifting bulkbags and for bottom discharge into an ion-exchange column or a storage vessel.

9. Economic Aspects

Commercial producers of synthetic spherical organic ion-exchange resins are listed in Table 2. Estimates for ion-exchange resin production are given from time to time, but must be viewed with a degree of uncertainty. Most sales are through distributors who may or may not be manufacturers of ion-exchange equipment. Purchase prices are determined by competitive bids or the distributors price list which may or may not be lower than the price suggested by the resin manufacturer.

Replacement sales have become an ever increasing percentage of total sales in the mature ion-exchange industry. Economic downturns such as that of the early 1990s affect resin purchases; plans for new installations are abandoned or delayed. Greater effort is made to forestall purchase of replacement resin by directing more attention to operating procedures, or by using chemical methods to restore old resin to a cleaner condition. In addition, quality improvement efforts by resin manufacturers have yielded products having greater physical durability, thereby lessening resin losses caused by physical attrition. Competitive technologies such as reverse osmosis (qv) have had an increasing impact on lowering the volume of resin required for old as well as new installations. Additionally, the once large installed volume of resin in the uranium [7440-61-1] industry has disappeared as environmental concerns over nuclear reactors (qv) have brought a halt to construction and operation of plants of this type, and as the cold war ended (see URANIUM AND URANIUM COMPOUNDS). On the positive side, a substantial growth of installed resin has occurred in processing corn sweetener for use in the beverage industry (see CARBONATED BEVERAGES; SWEETENERS). Significant growth has taken place in catalytic applications,

especially for the production of methyl *tert*-butyl ether [1634-04-4] (MTBE), a gasoline octane enhancer used in place of tetraethyllead [78-00-2].

Sales of cation-exchange resins have routinely been slightly more than twice the volume of anion exchangers, although deionization requires more anion exchanger than cation. Anion exchangers also have a shorter life and are replaced more frequently than cation exchangers. These factors are expected to favor greater sales of anion exchangers. One of the reasons for the opposite ratio is the large volume of cation exchangers used in homes and industrial plants for softening water. Another is the chromatographic separation of fructose [57-48-1] and glucose [492-62-6] in the corn sweetener industry which requires large volumes of cation-exchange resin. A similar process for recovery of sucrose [57-50-1] from beet sugar molasses added to the demand for cation exchangers. Catalysis (qv) by ion-exchange resins instead of conventional acids has also contributed substantially to the growth of cation exchangers in the petrochemical industry where resins are used for manufacture of MTBE, the hydrolysis of esters, and the hydration of olefins to form alcohols (see PETROLEUM).

Historically the United States was a primary exporter of ion-exchange resin. As of 1994, the United States imports substantially more than it exports. Because compliance with tightening environmental regulations in the United States impacts on the cost of manufacture, offshore resin is most often lower in price.

Cation exchangers range between \$2100 and \$3900/m³ (\$60–110/ft³). The average price of anion exchangers is about three times higher than that of cation exchangers. Anion-exchange resin production requires more steps than cation exchangers, and the chemicals used in production of anion exchangers are more expensive. The higher the degree of cross-linking for any resin, the greater the manufacturing cost. Macroporous resins command a higher price than microporous resins.

10. Specifications, Standards, and Storage

Resin manufacturers, equipment suppliers, consultants, and those using ion-exchange resins have worked cooperatively through ASTM to develop a set of standard procedures for measuring critical properties of the resins. Most laboratories use a version of these standards for quality control (qv) purposes, and to learn if any significant changes occur in resin properties after extended use. As more demanding requirements are developing for ultrahigh purity water in the power and electronics industries, additional methodology has been developing by organizations allied with those industries. Ion-exchange resins should be protected from freezing and from temperatures above 60°C. Resins, shipped water wet, should be stored in closed containers. If allowed to dry, they shrink. Rapid rewetting results in rapid swelling to the original water wet volume and contributes to bead breakage.

11. Health and Safety Factors

Ion-exchange resins are not considered hazardous. However, cation exchangers when in the hydrogen form, and anion exchangers when in the hydroxide form, yield acidic and basic solutions, respectively, when in contact with neutral salt solutions. The corrosive potential should not be overlooked, and skin sensitivity has been reported occasionally, especially when gloves are not used when handling resin. Resins which have been used to remove toxic substances may slowly release these materials if the toxic substances are still attached to the resin. Burning resins, if not incinerated properly, release toxic and odorous fumes. Fumes from burning anion exchangers are particularly foul smelling.

A few resins go through unusually large volume changes when converted from one ionic form to another, when changing from one solvent to another, or when wetting dry resin with water or another solvent. Such changes may cause shattering of glass equipment if constrained. Oxidizing chemicals in contact with ion-exchange resins can result in rapid and uncontrolled degradation which may lead to rupture or bursting of the column in an explosive manner. Moreover, resin beads spilled on a floor are especially dangerous and can be the cause of serious accidents resulting from falls.

12. Uses

12.1. Water Treatment. The two primary applications in water treatment are softening and deionization. Other important but less frequently used applications include dealkalization, softening of produced water, desilicizing, and nitrate removal.

Softening. The use of a cation-exchange resin in the sodium form to remove those ions that cause the water to be hard is called softening. Calcium [7440-70-2] and magnesium [7439-95-4] ions are the prime candidates. Other multivalent cations, such as iron, barium [7440-39-3], and manganese [7439-96-5] are also removed in the process. All are replaced with sodium [7440-23-5]. The softened water prevents problems such as scaling of pipes and heat exchangers. The resin is regenerated with NaCl, usually at a 10% concentration. A more costly alternative is potassium chloride [7440-40-7] when higher levels of sodium ions in the softened water are objectionable.

Problems common to water softening installations consist mostly of fouling by iron and removal of cross-linking from ion-exchange resins. Iron [7439-89-6] is present in water as iron(III) [20074-52-6], iron(II) [15438-31-0], and as colloidal iron oxides, depending on the source of the water. Iron hydroxides precipitate within the resin column when the soluble iron(II) is oxidized to iron(III). The NaCl solution used to regenerate the resin is not effective in dissolving precipitated iron. This results in its accumulation on the resin with each additional cycle. Pretreatment of water by chlorination leaves a residual of dissolved chlorine which, if greater than 0.1–0.3 mg/L, begins to oxidatively attack the resin by reducing cross-linking. The rate of cross-linking reduction intensifies as the

temperature increases, and when metals such as iron and copper that catalyze oxidative attack are present.

Deionization. The removal of cations and anions from water and replacement of them with hydrogen and hydroxide ions is called deionization. The completeness of the ionic removal is dependent on resin selection, design of the system, operating conditions, and the quality of treated water required. In general, systems become more complex as quality requirements increase.

Use of a strong acid cation exchanger and a weak base anion exchanger in a two-bed system yields the lowest quality water because the weak base resin cannot remove bicarbonate and silicate. That water is entirely satisfactory in numerous installations. If those ions must be removed, other systems such as those shown in Figure 7 produce water to meet requirements. Selecting an appropriate system is not easy and should be reviewed with engineers and consultants well versed in ion-exchange technology.

A problem common to deionization systems involves calcium sulfate precipitation in the cation unit when sulfuric acid is used in the regenerating solution at an excessive concentration or at an unfavorable flow rate. Organic fouling of anion exchangers is another common problem, especially when processing surface water supplies. The decay of leaves, bark, and other vegetation produces large and complex fulvic acid [479-66-3] and humic acids [1415-93-6], which are adsorbed by anion-exchange resins. Only a portion of them are removed during the short time available for regeneration. The result is a cycle to cycle accumulation within the resin particles. The rate of buildup varies from one resin type to another, depending on the structure of the copolymer used for its manufacture.

Dealkalization. An ion-exchange process that lowers the bicarbonate [71-52-3] concentration is termed dealkalization. It is used for those water supplies having a relatively high alkalinity or ratio of bicarbonate to sulfate and chloride also present in the water. Several techniques are available. A lime-zeolite system is a combination of chemical treatment and ion exchange. A lime slurry is added to the water, which may be at an elevated temperature, to precipitate most of the calcium and magnesium. A column containing a resin appropriate for softening water removes the residual calcium and magnesium. Systems running close to the boiling point of water are more aggressive with respect to the physical stability of the resin, especially when ambient temperature brine is used for regeneration of the resin.

Another dealkalization system is referred to as a split-stream process. A portion of the incoming water passes through a strong acid cation-exchange resin in the hydrogen form. All cations are removed resulting in an acidic effluent. The other portion of the influent is passed through a parallel column containing a strong acid cation exchanger in the sodium form. This column softens the water by removing calcium and magnesium, but has no effect on the alkalinity. The effluents from both columns are combined to form a neutral stream with much lower bicarbonate content.

Another alternative involves the use of a weak acid cation exchanger in the hydrogen form. This resin is not capable of removing all cations. It removes only the amount equivalent to the bicarbonate in the influent water. The acidity in the effluent stream is carbonic acid [463-79-6] which can be eliminated by installing a degasifier.

Anion-exchange resins are also capable of lowering alkalinity. A Type II strong base resin is preferred and is used in the chloride or mixed chloride-hydroxide form. Regeneration with a NaCl solution containing NaOH gives higher operating capacities than NaCl alone. A problem common to dealkalization is low operating capacity. This results in frequent regenerations.

Produced-Water Softening. In secondary-oil recovery projects involving steam injection to heat oil remaining in strata and to make it more fluid, the steam condenses and the water becomes contaminated with calcium, magnesium, and other salts (see PETROLEUM). This water is cycled back to steam generators after it is separated from the oil. However, severe scaling results if the water is not softened before the generator. Softening is a challenge because NaCl concentrations are usually in the several thousand mg/L range, or higher. The greater the Na^+ concentration with respect to Ca^{2+} and Mg^{2+} , the lower the degree of softening and the lower the operating capacity. At the lower total salt concentrations, two columns of strong acid resins are used in series. The second column acts as a polisher and is regenerated with an NaCl solution in an upflow situation. At higher total salt concentrations, a weak acid resin, which has greater selectivity for divalent cations, is used in place of the strong acid resin. At very high total salt concentrations, a chelate resin is used in place of the weak acid resin.

A problem common to produced water applications is the tendency for oil fouling of the resin. If weak acid or chelate resins are used, a two-step regeneration process is required which uses acid to remove calcium and magnesium from the resin, followed by a dilute NaOH solution to convert the resin to the sodium form.

Nitrate Removal. In those areas where nitrate [14797-55-8], NO_3^- , concentrations in the water supply have been close to or above allowable limits for potable water, nitrate removal is practiced. Strong base anion-exchange resins are used in the chloride form. The effluent must be carefully monitored since selectivity favors sulfate over nitrate. Processing water beyond an acceptable nitrate leakage can result in the nitrate concentration exceeding the influent concentration. Newer strong base resins functionalized with triethylamine, tributylamine, and other amines overcome this problem because the selectivity for nitrate is greater than sulfate (19,20). The resin is regenerated with a sodium chloride solution.

Condensate Polishing. Steam is recovered as condensate after passing through turbines, a process commonplace in the electrical power industry. During the process, small amounts of soluble and insoluble impurities appear in the condensate. Recycling the hot water, after removing impurities with mixed-bed resins, is far more economical than treating cold water sources. The rate of flow through the mixed-bed resin is much higher than in conventional water treatment because of the very low level of impurities. Two systems most frequently used are columns (deep beds) and thin layers of ground resin deposited on a pre-coat filter (powdered system). The process is called condensate polishing.

Boron Removal. Boron [7440-42-8] is occasionally present in water supplies at an unacceptable level. It cannot be removed with the standard anion-exchange resins unless the water is deionized. Selective removal is possible by using an anion exchanger functionalized with *N*-methylglucamine [6284-40-8].

This resin is in limited commercial supply. The borate form of conventional strong base anion exchangers is used in some nuclear reactors to adjust the concentration of boron in water used as a moderator. The resin releases boron as the water temperature rises.

12.2. Food Processing. The sugar and corn sweetener industries have the largest volume of installed ion-exchange resin in the food processing (qv) industry. Lesser quantities are used to process wine (qv), whey, fruit juices (qv), and gelatin (qv).

Sugar, or sucrose [57-50-1], is obtained from sugar cane as a juice by pressing cut canes, and from sugar beets by slicing the beets and extracting the sucrose with hot water. Organic and inorganic impurities must be removed from these extracts to obtain a white, crystalline product (see SUGAR).

Cane sugar factories produce a raw crystalline sucrose which is shipped to the refinery where the raw sugar is redissolved and impurities are removed by precipitation, bone char or granular carbon, ion exchange, and crystallization (qv). Resins are used for several purposes. Organic compounds responsible for color in sugar syrups are removed by char or carbon in most refineries. Additional removal is achieved by following the char or carbon system with columns of a strong base anion exchanger in the chloride form (21-23). There is a trend toward replacing char and carbon systems with resin for decolorization purposes. Deionization with a weak acid cation exchanger and a strong base anion exchanger is incorporated at those refineries desiring to produce a sucrose syrup with low color and a low ash content. A weak acid resin is selected over a strong acid resin to minimize conversion of sucrose to invert sugar (glucose and fructose). The soft drink industry, on the other hand, prefers invert sugar over sucrose as a syrup for sweetening purposes. Sucrose is inverted, or converted, to an approximate 50-50 mix of fructose and glucose by hydrochloric acid or a strong acid cation exchanger in the hydrogen form.

Beet sugar factories do not produce an intermediate raw, crystalline sucrose. Instead, the thin juice obtained from the beets passes directly through purification processes similar to those used by the cane sugar refineries. Ion exchange, as a processing step in beet sugar purification, is more common outside the United States. The U.S. beet sugar industry has, in recent years, made a more concerted effort to recover sucrose lost to molasses. Residual calcium and magnesium present in the molasses is first removed with a weak acid cation exchanger in the sodium form. The molasses is next passed through a strong acid cation exchanger in the sodium form. The functional groups of this resin slow down the forward movement of sucrose, but not sodium and potassium. The sucrose concentration builds up in zones as the molasses passes through the column. Water is fed alternately with molasses to aid in developing the separation. The hydrogen form of the resin cannot be used to remove sodium and potassium because the resulting acidity would convert a large portion of sucrose to a mixture of glucose and fructose.

Syrup derived from corn starch is called corn sweetener. Starch (qv) is converted to glucose enzymatically or by acid hydrolysis. Color, color precursors, and salts are removed by ion exchange. Most systems consist of several pairs of a strong acid cation exchanger followed by a weak base anion exchanger connected in series. The syrup, thus purified, is used in numerous food products. This same

purified syrup is enzymatically processed to convert a portion of the glucose to fructose. In a process similar to the recovery of sucrose from molasses, as mentioned above, glucose and fructose are separated chromatographically by using a strong acid resin. In this application, however, the resin is used in the calcium form. Glucose- and fructose-rich streams are recovered separately in the effluent and blended to form a high fructose corn sweetener (HFCS) which is of value to the beverage industry. It is similar to the invert syrup derived from sucrose.

Whey, a by-product in the manufacture of cheese, is deacidified and deionized using a two-bed system consisting of a strong acid cation exchanger followed by a weak base anion exchanger (24,25). A mixed bed of a strong acid cation and a strong base anion exchanger is included, at times, after the two-bed system to achieve a higher degree of purification.

Fruit juices can be deacidified with a weak base anion-exchange resin. Removal of compounds which cause a bitter taste is a more popular application (26,27). It is accomplished with resins that have no ion-exchange functionality. In essence, they are similar to the copolymer intermediates used by resin manufacturers in the production of macroporous cation and anion exchangers. These products are called polymeric adsorbents. They are excellent for removal of limonin [1180-71-8] and naringin [10236-47-2], the principal compounds responsible for bitterness in orange, lemon, and grapefruit juices. The adsorbents are regenerated with steam or alcohol. Decaffeination of coffee (qv) and tea (qv) is practiced with the same polymeric adsorbents (28).

Wines are processed by ion exchange for two purposes: excess acidity, which is responsible for tartness, is removed using a weak base anion exchanger (29,30); newly fermented wine is supersaturated with respect to potassium bitartrate [868-14-4] and, unless the concentration is reduced, a precipitate eventually forms. Precipitation is hastened in the traditional method of processing wine by storing it at a lower temperature (chill-proofing). The sediment is periodically removed (racking) (31). The chill-proofing process is substituted with an ion-exchange process at numerous wineries. Precipitation is prevented by converting a portion of the potassium bitartrate to the more soluble sodium bitartrate [526-94-3] when passing the wine through a strong acid cation exchanger in the sodium form.

12.3. Pharmaceutical. Ion-exchange resins are useful in both the production of pharmaceuticals (qv) and the oral administration of medicine (32). Antibiotics (qv), such as streptomycin [57-92-1], neomycin [1404-04-2] (33), and cephalosporin C [61-24-5] (34), which are produced by fermentation, are recovered, concentrated, and purified by adsorption on ion-exchange resins, or polymeric adsorbents. Impurities are removed from other types of pharmaceutical products in a similar manner. Resins serve as catalysts in the manufacture of intermediate chemicals.

Ground ion-exchange resins have been used for many years as carriers for drugs which are ingested (see DRUG DELIVERY SYSTEMS). This method of dosing overcomes objectionable odors and tastes. Resins, especially those having strong acid or base functionality, provide slow (or sustained) release over many hours for those medicines adsorbed by them. A low cross-linked modification of a strong base styrene-divinylbenzene resin is dried and ground, then ingested for adsorption of bile acids in the treatment of people having high levels of blood cholesterol

[57-88-5]. The pharmaceutical generic name for this resin is cholestyramine [11041-12-6]. A hemoperfusion system incorporating a polymeric adsorbent was developed to adsorb drug and drug metabolites from the blood of patients who had overdosed (see CONTROLLED RELEASE TECHNOLOGY, PHARMACEUTICAL).

12.4. Catalysis. Ion-exchange resins, especially the strong acid type, have long been recognized as excellent substitutes for sulfuric acid and other similar catalytic agents. Resins participate in fewer side reactions, and because they are insoluble, remain in the reactor and do not contribute to downstream corrosion problems. Neutralization of the reaction product is not necessary. Regeneration of a resin catalyst is not required unless the incoming reactant streams contain impurities that would be adsorbed by the resin. Separate ion-exchange units are used, at times, to remove the impurities from those streams before they enter the reactor. Numerous large reactor columns have been designed and installed in the petrochemical industry which have no facilities for regeneration. Resin is replaced when performance drops off, which may be well over one to two years of continuing operation.

An etherification reaction to form methyl *tert*-butyl ether [1634-04-4] (MTBE), $\text{CH}_3\text{OC}(\text{CH}_3)_3$, used as an octane enhancer in gasoline, has become the most widely used application in catalysis by ion-exchange resins and incorporates the largest sized reactors (35,36). The entering methanol and isobutylene [115-11-7] streams are essentially free of impurities. Mole ratios of the reactants and operating temperatures are site specific. The reaction temperature is gradually increased as the resin ages. The preferred catalyst for this reaction is a strong acid-type resin having macroporous properties. The same type catalyst is used in the hydration of olefins to form alcohols, the alkylation of phenols, and the hydrolysis of esters. Microporous catalysts are preferred for the manufacture of bisphenol A [80-05-7], esterification reactions, and in alkylation of phenol [108-95-2]. Macroporous catalysts are also used in several of these processes. At times, it is advantageous to convert the functional groups to other forms, as in the adsorption of platinum [7440-06-4] and palladium [7440-05-3], for example.

12.5. Chemical Purification. Many organic and inorganic products manufactured in commercial quantities contain objectionable impurities which can be removed by ion exchange. Selection of the appropriate resin is important. Iron(III) is removed from hydrochloric acid using a strong base anion exchanger (see HYDROGEN CHLORIDE). Divalent cations, eg, calcium, magnesium, strontium, and barium, are removed from saturated NaCl solutions or other monovalent salt solutions using chelate resins (37). Formic acid is removed from hot, concentrated formaldehyde [50-00-0] using a weak base anion exchanger. Amines are removed from methanol [67-56-1] using a strong acid-type cation exchanger. Salts are removed from dimethylformamide [68-12-2] with a strong acid cation exchanger followed by a weak base anion exchanger. Gelatin (qv) [9000-70-8] is purified in a similar manner, although a strong base anion exchanger is generally preferred over a weak base resin. Oxazole [288-42-6] is removed from acrylonitrile (qv) [107-13-1] using a strong acid resin.

Ion exclusion and ion retardation are single-resin systems which separate electrolytes from nonelectrolytes without the normal type of adsorption occurring. Ion-exchange resins exclude a fraction of electrolyte from the resin phase because of the Donnan membrane equilibrium principle. This principle

requires equal electrochemical potentials for the permeating ions on each side of the membrane. A column of cation- or anion-exchange resin, with the functional groups in the same ionic form as the cations or anions in a feed stream containing an electrolyte and a nonelectrolyte, excludes most of the electrolyte and slows forward movement of the nonelectrolyte. Separation is achieved by alternating feed of water with the electrolyte or nonelectrolyte stream. Regeneration is not required.

Ion retardation is the opposite of ion exclusion. Instead of using a resin with all sites having the same structure and being in the same ionic form, ion retardation involves a resin which contains both cation and anion functionality. These resins are not widely available commercially. The functional sites are in very close proximity of each other, and partially neutralize the positive and negative charges of the groups. Cations and anions, present in a feed stream containing electrolytes and nonelectrolytes, are loosely held by the functional groups. They are retarded in their forward motion, while the nonelectrolyte passes through the resin bed at a slightly faster rate. Like ion exclusion, water is fed alternately with the feed stream, and regeneration is not required. In both systems, water displaces the nonelectrolyte, or electrolyte, that was restrained in its forward movement by the resin.

12.6. Metal Processing. Plating, etching, anodizing, pickling, and galvanizing involve chemical solutions or baths that are used repeatedly until the impurity concentration increases to a level where additional use of the bath impairs performance. Destruction of the bath is costly and creates a disposal problem. Ion-exchange units are installed at numerous locations to lower the impurity concentration to an acceptable value. Complete removal is not necessary. Examples include the removal of iron, copper, and trivalent chromium(III) from chromic acid [1333-82-0] plating baths (38), the removal of copper from etching solutions (39,40), the removal of aluminum [7429-90-5] from anodizing baths (41), removal of iron from pickling acids, and removal of iron from acidic zinc sulfate [7733-02-0] ZnSO_4 galvanizing baths (42). Resin selection is critical for success of the process (see ELECTROPLATING; METAL TREATMENTS).

12.7. Hydrometallurgy. Uranium [7440-61-1] recovery from sulfuric acid leaching (43-46) and bicarbonate leaching (47,48) operations involved the largest use of ion-exchange resins in the hydrometallurgical area (see METALLURGY, EXTRACTIVE). Activity was at its peak in the 1970s. Many of the mill sites shut down when the demand for uranium in the arms race and in nuclear reactors for generation of power declined. The volume of resin installed in the United States, Canada, and the Republic of South Africa is not likely to be matched in any hydrometallurgical application in the future.

Uranium ores are leached with dilute sulfuric acid or an alkaline carbonate [3812-32-6] solution. Hexavalent uranium forms anionic complexes, such as uranyl sulfate [56959-61-6], $\text{UO}_2(\text{SO}_4)^{-2}$, which are more selectively adsorbed by strong base anion exchangers than are other anions in the leach liquors. Sulfate complexes are eluted with an acidified NaCl or ammonium nitrate [6484-52-2], NH_4NO_3 , solution. Carbonate complexes are eluted with a neutral brine solution. Uranium is precipitated from the eluent and shipped to other locations for enrichment. Columnar recovery systems were popular in South Africa and Canada. Continuous resin-in-pulp (RIP) systems gained popularity in the United

States since they eliminated a difficult and costly ore particle/leach liquor separation step.

Other hydrometallurgical uses for resin have been small in comparison. Replacement of carbon as an adsorbent for gold [7440-57-5] from a cyanide [57-12-5] leached ore has been studied for many years, but remains in limited commercial use. A deterrent has been the failure to develop an efficient and safe method to recover gold from the resin. Gold forms an anionic cyanide complex which is readily adsorbed by a strong base anion exchanger (49,50). A program has been underway in South Africa to use weak base anion exchangers (phenolics have shown greatest promise), but since these resins are more sensitive to pH above 7.0, loading capacity is not as high as with strong base resin or carbon. Strong acid resins were installed for the commercial separation of rare earths (see LANTHANIDES). Nickel [7940-02-0] and cobalt [7440-48-4] were separated and purified with an iminodiacetic acid [142-73-4] type chelate resin. Niobium [7440-03-1] has been separated from other metals by forming anionic fluoride complexes and passing the solution through a strong base anion exchanger. Bromine [7726-95-6] and iodine [7553-56-2] are recovered from seawater and other brines by adsorption of bromate [15541-45-4] or iodate [15454-31-6] on a strong base resin.

12.8. Waste Treatment. Environmental concerns have increased the need to treat liquid discharges from all types of industrial processes, as well as runoffs where toxic substances appear as a result of leaks or following solubilization (see WASTES, INDUSTRIAL). One method of treatment consists of an ion-exchange system to remove the objectionable components only. Another involves complete or partial elimination of liquid discharges by recycling streams within the plant. This method is unacceptable unless a cyclic increase in the impurities is eliminated by removing all constituents prior to recycling.

In the first approach, numerous toxic metals are lowered below discharge limits through use of the standard cation- and anion-exchange resins, or by using specially formulated resins which have much higher selectivities. For example, chromium(III) [16065-83-1] in a rinsewater or a groundwater is adsorbed on a strong acid cation exchanger (51). Chromium(VI) [18540-29-9] is adsorbed on a strongly basic anion exchanger. Copper is adsorbed more completely from an ammonium sulfate [7783-20-2] solution by chelate resins than by the standard cation exchangers. A resin containing thiol (SH^-) functionality has very high selectivity for mercury [7439-97-6], and other metals which form sulfide precipitates (52,53). Selective removal is preferred for leachates common to existing and abandoned mine sites, holding ponds, land fills, and lagoons.

Recycling systems incorporate cation and anion exchangers to remove all electrolytes. Other nontoxic material, common to the process, appear in the process water along with the toxic substances and, unless removed, lower the quality of the water. By using a cation- and anion-exchange resin system, the water produced will be of higher quality than water normally available to the facility. Deionization of recycled water is less costly if the electrolyte concentration is lower than in external water supplies. If the concentration is greater in recycled water, elimination of streams with high electrolyte concentrations and free of toxic substances should be considered. Recycling lowers regeneration chemical

costs and minimizes the volume of water that must be purchased from an external source.

Numerous organic compounds cannot be removed efficiently with ion-exchange resins or polymeric adsorbents, but others can. Low molecular weight organic acids and bases are adsorbed by anion and cation exchangers, respectively. Whereas higher molecular weight compounds might be adsorbed satisfactorily, they do not desorb easily during regeneration. Polymeric adsorbents are excellent materials for the removal of phenolic-type compounds (54).

Removal of radioactive ions is accomplished with standard resins when selectivities are favorable and when the presence of other electrolytes does not interfere. Deionization systems are common when completeness of removal is essential.

Toxic substances adsorbed on resins are removed during a regeneration procedure. The resulting spent regeneration solution has a higher concentration of the toxic substance than the stream from which it was removed by the resin. Toxic material in the spent regenerating solution can usually be precipitated, electrodeposited as in an electrolytic cell, or made insoluble by other acceptable procedures.

12.9. Gas Adsorption. There are few commercial installations. Ammonia [7664-41-7] is adsorbed by a cation exchanger in the hydrogen form and eluted with an acid to give ammonium sulfate or ammonium chloride [12125-02-9]. Success has been reported on the removal of sulfur dioxide [7446-09-5] on a weak base anion exchanger (55) (see ADSORPTION, GAS SEPARATION). Chemical compounds such as phenol, ethylene dichloride [107-06-2], and benzene [71-43-2] have been successfully removed on polymeric adsorbents (56). The concern with systems for removing impurities from air, or other gaseous streams, is the high pressure drop typical of high velocities through beds of small-diameter resin particles. Other concerns are water content of both the resin and the gaseous stream, temperature, and cost effective regeneration procedures, especially for organic substances.

12.10. Analytical. Ion-exchange resins have been extremely valuable for a variety of analyses. Total ion electrolyte concentration can be determined by analyzing for total cations or total anions using a cation exchanger in the hydrogen form or an anion exchanger in the hydroxide form. Ions present in solution at very low concentrations are concentrated by adsorption on a resin before eluting and analyzing the effluent by standard procedures. Ions that are interferences for analytical procedures are eliminated by adsorption on an ion exchanger. The progress of a large-scale plant reaction can be monitored by following the disappearance of a reactant. Impurity levels in a finished product are determined by ion exchange if it is adsorbable. Numerous commercial processes have evolved from analytical separations and purifications practiced in the laboratory as an analytical procedure.

Ion chromatography (ic) is a highly valued and growing methodology for analytical analysis of ionic constituents in aqueous streams. In contrast to the chromatographic separations mentioned earlier with conventional resins, ion chromatography uses similar, yet different, resins which yield separations that are measured in minutes, rather than hours and days (see CHROMATOGRAPHY). Resins are somewhat smaller in size and have most of the functional groups

on or near the outer surface, in contrast to being distributed throughout the resin matrix in conventional resins. The outer surface functionality shortens the path from liquid phase to resin phase and is the factor not only for more rapid separations, but also separations with little overlap in peaks for separate ions. With functionalization limited to the outer shell, the capacity of the resin is significantly reduced. Ion chromatography is generally considered for the more dilute streams where concentrations extend down to the mg/L and $\mu\text{g/L}$ ranges. Ion chromatography resins are placed in a narrow separator column which is followed by a suppressor column and an analytical instrument to pick up signals in the effluent stream. Separate systems are used for cations and anions.

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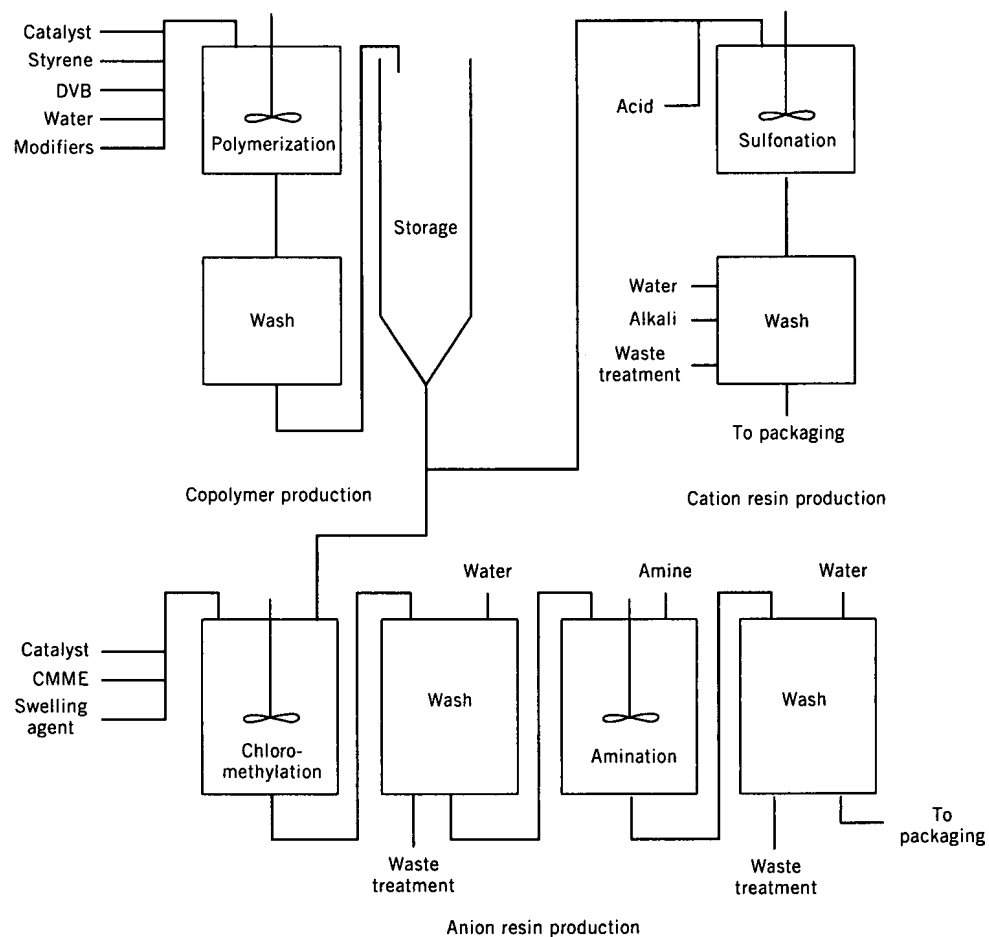


Fig. 1. Ion-exchange production schematic. CMME is chloromethyl methyl ether.

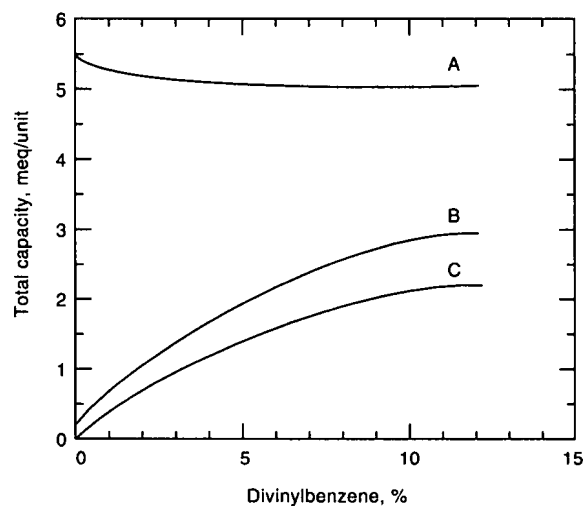


Fig. 2. Total capacity vs cross-linkage for polystyrene sulfonic acid resin in the H^+ form where A and B correspond respectively to dry and wet weight capacity in meq/g of resin, and C represents wet volume capacity in meq/mL of wet settled resin.

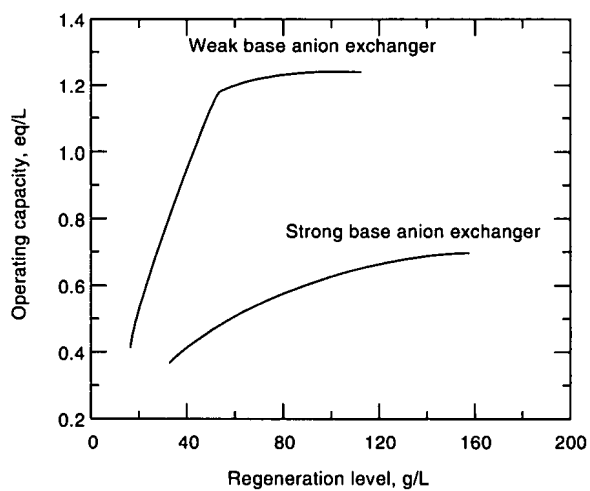


Fig. 3. Regeneration of anion-exchange resins using NaOH (14).

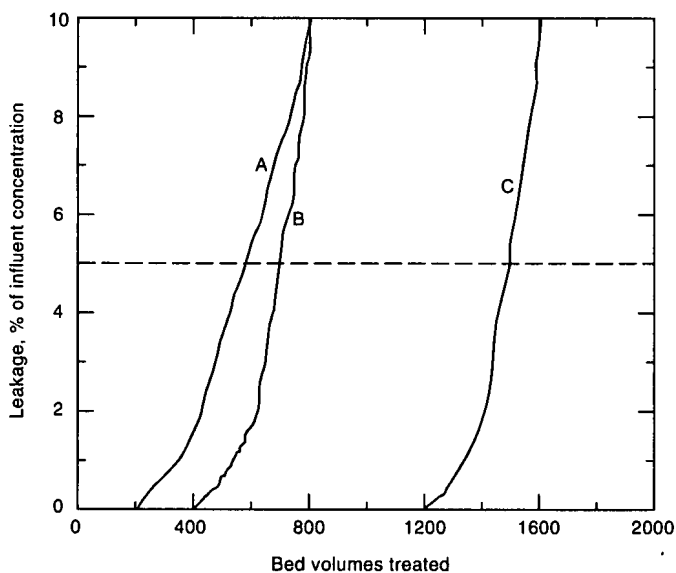


Fig. 4. Hypothetical leakage curves to show effect of ionic concentration and flow rate, where the dashed line corresponds to the leakage shutdown level for regeneration. See text.

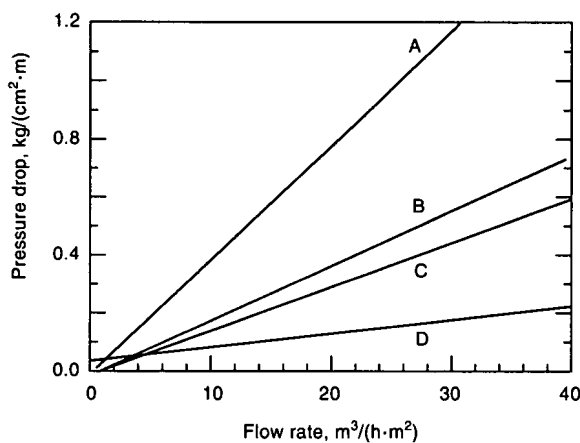


Fig. 5. Pressure drop as affected by resin type, flow rate, and temperature, where A, B, and C, correspond respectively to acrylic strong base anion exchanger (Amberlite IRA-458), styrenic strong base anion exchanger (Amberlite IRA-402), and styrenic strong acid cation exchanger (Amberlite IR-120), all at 4°C. D represents styrenic strong acid cation resin (Amberlite IR-120) at 50°C (14). To convert $\text{kg}/(\text{cm}^2 \cdot \text{m})$ to $\text{lb}/(\text{in.}^2 \cdot \text{ft})$, multiply by 4.33; to convert $\text{m}^3/(\text{h} \cdot \text{m}^2)$ to $\text{gal}/(\text{min} \cdot \text{ft}^2)$, multiply by 0.409.

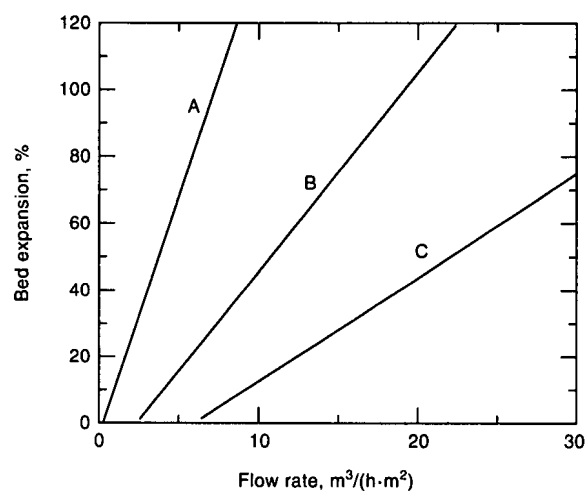


Fig. 6. Bed expansion as affected by resin type, flow rate, and temperature, where A represents a strong base styrenic resin in the Cl^- form at 4°C , and B and C a strong acid styrenic resin in the Na^+ form at 4 and 50°C , respectively (14). To convert $\text{m}^3/(\text{h} \cdot \text{m}^2)$ to $\text{gal}/(\text{min} \cdot \text{ft}^2)$, multiply by 0.409.

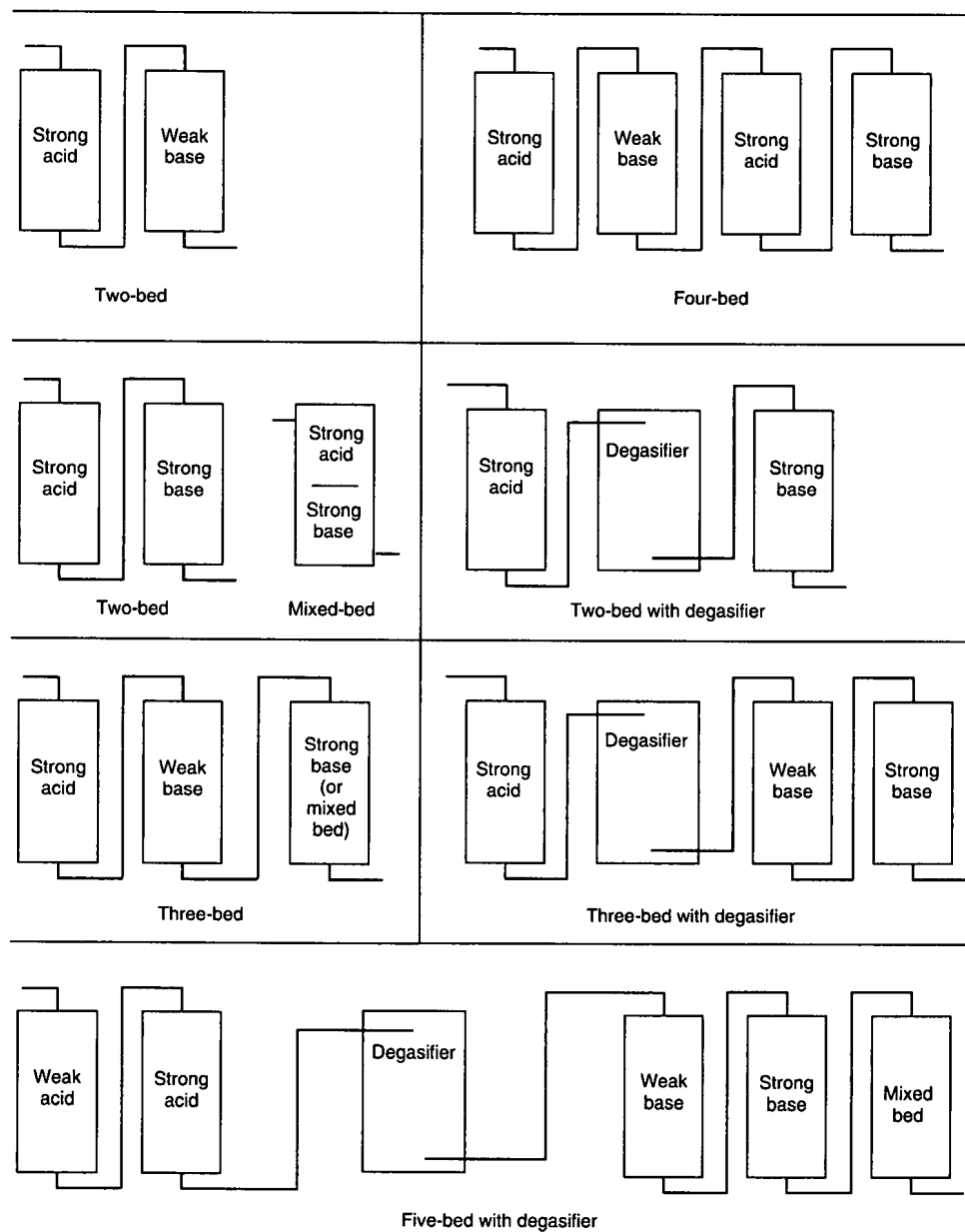


Fig. 7. Various deionization systems. A degasifier facilitates the removal of dissolved gases.

Table 1. Selectivity for Anions on Anion Exchangers^a

Ion	CAS Registry number	Dowex 1 ^b		Dowex 2 ^c		Dowex 2 ^c	
		X_{Cl}	K_{Cl}	X_{Cl}	K_{Cl}	X_{Cl}	K_{Cl}
iodide	[20461-54-5]	0.27	8.7	0.27	7.3	0.07	13.2
nitrate	[14797-55-8]	0.38	3.8	0.36	3.3	0.34	3.3
nitrite	[14797-65-0]	0.51	1.2	0.52	1.3		
hydroxide	[14280-30-9]	0.77	0.09	0.56	0.65		
bicarbonate	[71-52-3]	0.65	0.32	0.63	0.53		
formate	[71-47-6]	0.70	0.22	0.68	0.22		
fluoride	[16984-48-8]	0.77	0.10	0.76	0.10		

^aSelectivity is vs that for Cl^- . Mol fraction of Cl^- , X_{Cl} , is given.^bType I functionality.^cType II functionality.

Table 2. Commercial Producers

Company	Country	Trade name(s)
Bayer	Germany	Wofatit, Lewatit
Chemolimpex	Hungary	Varion
Dow	United States, Italy, Germany	Dowex
Mitsubishi Kasei	Japan	Diaion
Ostion	Czechoslovakia	Ostion
Purolite	United States, Wales, Romania	Purolite
Röhm and Haas	United States, France, Japan	Amberlite, Amberlyst, Duolite
Sybron	United States	Ionac